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**Quarterly Progress Report for the
Chemical and Energy Research Section
of the Chemical Technology Division:
January–March 1999**

R. T. Jubin

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE
CHEMICAL AND ENERGY RESEARCH SECTION OF
THE CHEMICAL TECHNOLOGY DIVISION:
JANUARY-MARCH 1999

R. T. Jubin

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ACRONYMS

ACB	auxiliary charcoal bed
BTEX	benzene, toluene, ethylbenzene, and xylenes
CBD	cellulose-binding domain
CST	crystalline silicotitanate
CSTR	continuously stirred tank reactor
CV	column volumes
DF	decontamination factor
DI	deionized
DLS	dynamic light scattering
DOE	U.S. Department of Energy
EHD	electrohydrodynamic
EMSP	Environmental Management Science Program
EPRI	Electric Power Research Institute
ESP	Environmental Simulation Program
FTIR	Fourier transform infrared
GDH	glucose dehydrogenase
HFIR	High Flux Isotope Reactor
HLW	high-level waste
HPLC	high-performance liquid chromatography
ICP-AE	inductively coupled plasma-atomic emission
LED	light-emitting diode
MSRE	Molten Salt Reactor Experiment
MST	monosodium titanate
MVST	Melton Valley Storage Tank
NaTPB	sodium tetraphenylborate
NERSC	National Energy Research Supercomputing Center
NMR	nuclear magnetic resonance
NSF	National Science Foundation
NTS	Nevada Test Site
ORNL	Oak Ridge National Laboratory
PCR	polymerase chain reaction
PSI	Photosystem I
RCRA	Resource Conservation and Recovery Act
RMAL	Radioactive Materials Analytical Laboratory
SALS	small-angle light scattering
SAMs	self-assembled monolayers
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
TFA	Tanks Focus Area
TPB	tetraphenylborate
TRU	transuranic
TTCF	transient time correlation function
WAC	waste acceptance criteria
WTP	Waste Triad Project
XRD	X-ray diffraction

EXECUTIVE SUMMARY

This report summarizes the major activities conducted in the Chemical and Energy Research Section of the Chemical Technology Division at Oak Ridge National Laboratory (ORNL) during the period January–March 1999. The section conducts basic and applied research and development in chemical engineering, applied chemistry, and bioprocessing, with an emphasis on energy-driven technologies and advanced chemical separations for nuclear and waste applications.

The report describes the various tasks performed within eight major areas of research: Hot Cell Operations, Process Chemistry and Thermodynamics, Molten Salt Reactor Experiment (MSRE) Remediation Studies, Chemistry Research, Separations and Materials Synthesis, Fluid Structure and Properties, Biotechnology Research, and Molecular Studies. The name of a technical contact is included with each task described, and readers are encouraged to contact these individuals if they need additional information.

Activities conducted within the area of *Hot Cell Operations* included column loading of cesium from Melton Valley Storage Tank supernatants using an engineered form of crystalline silicotitanate. A second task was to design and construct a continuously stirred tank reactor system to test the Savannah River–developed process of small-tank tetraphenylborate precipitation to remove cesium, strontium, and transuranics from supernatant.

Within the area of *Process Chemistry and Thermodynamics*, the problem of solids formation in process solutions from caustic treatment of Hanford sludge was addressed, including issues such as pipeline plugging and viscosity measurements. Investigation of solution conditions required to dissolve Hanford saltcake was also continued.

MSRE Remediation Studies focused on recovery of ^{233}U and its transformation into a stable oxide and radiolysis experiments to permit remediation of MSRE fuel salt.

In the area of *Chemistry Research*, activities included studies relative to molecular imprinting for use in areas such as selective sorption, chemical sensing, and catalysis, as well as spectroscopic investigation into the fundamental interaction between ionic solvents and solutes in both low- and high-temperature ionic liquids.

In the area of *Separations and Materials Synthesis*, fundamental studies explored the use of electromagnetic fields to enhance transport processes in multiphase separations; investigated nucleation and particle growth for the synthesis, characterization, application, and processing of ultrafine particles; and examined the use of electric fields to modify phase equilibria in multiphase separations processes. Other efforts involved enhanced oxidation of organic pollutants in aqueous solutions by applying electric fields to form microbubbles and the use of electric fields to improve distillation efficiency. Research was also directed toward the use of ozonation to treat water-soluble organics, the application of electrical and acoustic methods to remediate aerosol problems, and the development of improved means of decontamination using aqueous surfactant cleaners.

Fluid Structure and Properties included molecular-based studies of systems with supercritical solvents, a multi-institutional initiative to develop a molecular understanding of reverse miscelles in supercritical carbon dioxide through experimentation and molecular simulation calculations, and molecular-based prediction of the structure and properties of long-chain molecules undergoing shear flow.

Within the area of *Biotechnology Research*, tasks included research into fundamental reactions of photosynthesis, investigation of renewable hydrogen production by photosynthetic water splitting, and development of fluorometric tissue-based biosensors. In enzyme-related work, studies were undertaken to improve biocatalysts by increasing the catalytic rate of hydrolysis of cellulose and to increase the efficiency of enzymatic production of hydrogen from glucose. Work on non-enzymatic production of hydrogen from an iron-powder catalyst continued.

In the final area—*Molecular Studies*—as part of an effort to enhance our microscopic-level understanding of aqueous electrolyte solutions, molecular dynamics simulations of supercooled water were performed. The investigation of simulation algorithms for nonequilibrium systems continued, and work on an integral equation theory for such systems was concluded. The completed project on modeling in situ bioremediation processes continued to generate publications. The Chialvo-Cummings solvation formalism was applied to electrolyte solutions, significant progress was made in parallel implementations of the Geocore algorithm, and large-system production runs were conducted of the simulation code for reverse miscelles. In addition, molecular dynamics simulations of alkanes confined to nanoscale gaps were conducted.

1. HOT CELL OPERATIONS

E. C. Beahm

1.1 CESIUM REMOVAL USING CST IN SUPPORT OF THE MELTON VALLEY WASTE TRIAD PROJECT (WTP 1, 2, AND 3) (CRC1, CRC2, AND CRC3 RESULTS) (D. D. Lee and C. W. Chase)

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Summary: Three tests were completed in support of the Waste Triad Project (WTP) in Melton Valley. These tests utilized the supernatant from Melton Valley Storage Tanks (MVSTs) W-29, W-30, and W-31 in ion-exchange columns containing UOP IE-911 crystalline silicotitanate (CST) that is being used in the cesium-removal portion of the Triad. The tests loaded cesium from the supernatants onto the CST, and the loaded sorbents were transferred to the Building 2026 Radioactive Materials Analytical Laboratory (RMAL) for testing to ensure compliance with Nevada Test Site (NTS) acceptance requirements. Each column was loaded to the approximate level of cesium per unit of CST that is planned for the Melton Valley columns, and the breakthrough curves for cesium were determined at a flow rate of 12 column volumes (CV)/h. The testing showed no compliance problems for any of the supernatants tested, and operation was predictable and consistent for all tests.

1.1.1 Purpose and Scope

Oak Ridge National Laboratory (ORNL) served as the pilot plant for the Hanford production facility during the 1940s. As a result, the waste contained in the ORNL storage tanks is similar to waste found at other sites, but it is typically 10 to 100 times less radioactive. It is estimated that nearly 4.9 million liters of legacy waste is stored on-site at ORNL. Of this volume, about 20% is transuranic (TRU) sludges, and the remainder is classified as low-level waste. The waste contains approximately 130,000 Ci, composed primarily of ^{137}Cs , ^{90}Sr , and small amounts of other fission products. The wastes were originally acidic in nature but were neutralized using Na_2CO_3 , NaOH , or CaO to allow their storage in tanks constructed of carbon steel or concrete (gunite). In addition to the legacy waste, about 57,000 L of concentrated waste is generated annually, which contains about 13,000 Ci, consisting primarily ^{137}Cs , ^{90}Sr , and small amounts of other fission products.

The description of this task includes the operation of the experimental test unit that is located in Building 4501 (hot cell C) and the results using the CST sorbent tested. The Efficient Separations and Processing Crosscutting Program and the Tanks Focus Area (TFA) have utilized the information from these studies to transfer the technologies being developed to end users through the Accelerated Site Technology Deployment Program. Before the WTP is operated using these

supernatants, the parallel tests conducted using this equipment will provide an evaluation of the performance and loading that can be expected in the large system. The WTP is designed to filter, remove cesium, and concentrate the supernatant before it is transferred to the new-capacity tanks in Melton Valley. It also provided loaded sorbent material for evaluation with regard to waste acceptance criteria (WAC) and TRU loading.

1.1.2 Progress

1.1.2.1 Experimental Systems, Procedures, and Tests

The bench-scale tests are conducted in small columns using 10–17 cm³ of CST sorbent added as a slurry to the 1.5-cm-ID column. The column is attached to hot cell C system in Building 4501. The MVST supernatant is pumped through a 0.45- μ m filter to the feed tank and then down through the column at a flow rate to match that of the planned volumetric flow in the WTP (i.e., 12 CV/h in the first three tests). The effluent from the column is monitored for ¹³⁷Cs using an in-line sodium iodide detector, and a fraction collector is used to collect all of the effluent in approximately 200- to 240-mL portions. The test normally continues until the in-line detector shows that the desired ¹³⁷Cs loading on the column has been achieved. The loading is confirmed by counting the effluent fractions before ending the run. Based on the breakthrough curve and the samples analyzed, an estimate of the curie loading on the column is then made.

As part of the sorbent qualification procedure, the column with cesium-loaded sorbent is sent to the RMAL for Toxicity Characteristic Leaching Procedure (TCLP) analysis to determine if the sorbent is Resource Conservation and Recovery Act (RCRA) hazardous. The sorbent analyses will determine if the loaded CST is a characteristic hazardous waste (under 40 CFR 261, subpart C) by analyzing the TCLP extract solution for the RCRA hazardous metals. Some of the sorbent will also be dissolved, and the amount of TRU material loaded will be determined.

1.1.2.2 Continuous Hot Cell Experimental System

The sorbents were tested using 1.5 by 15- to 20-cm columns containing about 10–17 cm³ of sorbent at flow rates of 12 CV/h. The breakthrough of cesium from the sorbent was followed by an on-line gamma spectrometer, and the effluent was also fractionated for chemical and radiological analyses. Sorbents were also analyzed after removal from the cell by the RMAL, which is approved for NTS analyses.

1.1.2.3 Supernatants Tested in the Experiments

The MVST supernatants from tanks W-29 and W-30 were the first to be used in the companion runs with the WTP. The ^{137}Cs levels of W-29 and W-30 were between 5.2 and 10×10^5 Bq/mL.

1.1.2.4 Batch Tests

Granular CSTs were developed by Sandia National Laboratories and Texas A&M University and supplied by UOP as IONSIV® 911. Batch contact tests were conducted before the column tests to get a prediction of the breakthroughs. A brief discussion of the batch test results follows.

For the batch tests of W-29, W-30, and W-31 with the CST, duplicate tubes were prepared for analysis after 24 and 96 h of shaking (72 h for W-31) with about 10 mL of supernatant and 50 mg of CST in each tube. Additional tube blanks for both sample times were also prepared without the CST. The CST used for the batch tests with W-29 and W-30 was from the UOP IE-911 -0004 batch, previously prepared by WTP at Building 2528 and air dried. Batch -0005 for W-31 supernatant was used as received. No further preparation of either sorbent was done. Approximately 2-mL samples from each tube were filtered through a 0.2- μm filter and then counted for ^{137}Cs .

The preceding tests were analyzed by calculating the distribution coefficient, called the K_d or D value. The K_d is calculated according to the formula

$$K_d = (C_0/C - 1) V/m,$$

where C and C_0 are the starting and final cesium concentrations, respectively; V is the volume of solution in contact with the sorbent (in milliliters), and m is the mass (as received) of CST (in grams). This can be adjusted to the dry weight of CST to compare with other samples if the ratio of dried weight to the as-received weight is determined. The capacity of the sorbent can be estimated by multiplying the K_d by the bulk density of the sorbent, ρ (1.100–1.130 for our batch of CST), giving λ , an estimate of the number of column volumes of liquid that a column can process prior to reaching a 50% breakthrough of the cesium in the column effluent: $\lambda = K_d \cdot \rho$. Additional calculations that can be made include the percent removal of cesium, $[(C_0 - C)/C_0 \times 100]$, and the decontamination factor (DF).

1.1.2.5 Small-Column Cesium-Removal Operation

The system is operated continuously with on-line monitoring of the column effluent to detect ^{137}Cs breakthroughs from the sorbent in the column. Once the column was loaded, it was disconnected from the experimental system and removed from the cell for analysis. The column product stream was collected in the fraction collector, and samples of these fractions were counted

using an EG&G ORTEC Model GMX-45220-P-S PopTop Gamma-X system with an EG&G ORTEC Model 672 spectroscopy amplifier, Canberra Accuspec-A multichannel analyzer card, and Canberra GENIE-2000 Gamma Analysis software. The detection limit for the ORTEC system is about 0.005% of the feed concentration, when the low-activity samples were counted for up to 18 h. Samples were counted on the ORTEC system at 30 cm from the detector head, and the system was calibrated with an NTIS SRM-4275C counting standard.

1.1.2.6 CRC1 (WTP1) Qualification of CST and MVST W-30

The ion-exchange columns were prepared on the day the run started. The CST was delivered to Building 4501 in a 250-mL plastic bottle labeled IONSIV IE-911, lot no. 99909681004. The CST had been pretreated to pH 12.6 with caustic at Building 2528, was in air-dried form, and was taken directly from the plastic bottle and placed in the column. The sorbent was at a level of 10.3 cm of CST and tapped with the corresponding volume of 16.9 mL. The bed was fluidized to remove fines by using 15 CV of deionized (DI) water first to wet the CST, followed by 0.6 *N* NaOH and then 5 CV of DI water (because the supernatant was almost neutral pH). The initial flow was milky and left numerous fines in the drain bottle. After pretreatment, the settled bed height was 10.3 cm. The liquid in the column was then lowered to about 1 cm above the bed, and the column was secured for transfer to the cell after adding the top tubing connections and clamping the inlet and outlet tubes with pinch clamps.

One of the combined bottles of feed (mixed by pouring the contents of the two bottles together from one to the other a total of five times) was prepared to pump supernatant to the system feed tank and was pumped at a flow rate of about 35–40 mL/min. Transfer of the 2 L of supernatant required about 60 min. After the transfer was complete, the pump was set to operate with the level controller in the feed tank. When the level decreased by about 200 mL, the pump restarted and refilled the tank.

The fraction collector was prepared by placing empty 250-mL polypropylene bottles in the nine positions, and setting the program for remote operation. It was expected that approximately 1 h of pumping through the column would place about 190–200 mL of treated supernatant in each bottle at the test design of about 2 mL/min (12 CV/h).

When all preparations had been completed, the feed pump and valves were configured to pump supernatant to the bubble-trap column and, from there, through the CST column to the detector and the fraction collector. After about 3 CV, the rate was fairly stable; after 6 CV, there was very little variation throughout the rest of the loading operation.

The cell-detector data collection and the fraction collector were started after it had been determined that liquid had passed through the detector. No problems were encountered after flow was completely established through the pump and columns at the desired flow rate. The run was completed uneventfully to 404 CV (34 h), after 6.2 L of supernatant had been fed.

The loading was continued until approximately 171 mCi of ^{137}Cs had been fed to the column. This represents a total of 4348 Ci/m³ CST and is below the Class C limit of 4600 Ci/m³, taking into account both columns of the two-columns-in-series operating plan. This loading occurred at 404 CV and about 2.72% breakthrough. The loading was determined by subtracting the concentration in the column effluent from the feed concentration and assuming that the difference was loaded on the column. Following the run, samples were analyzed to make the final determination of the extent of loading. Results from the ^{137}Cs samples and the cell-detector output were in very good agreement. The sample ^{137}Cs analyses breakthrough was 2.7% at the end of loading. The sorbent from the loaded column was subjected to a modified TCLP procedure and showed all levels in the leach liquid were below the regulatory limits.

1.1.2.7 CRC2 (WTP3) Qualification of CST and MVST W-29

In test CRC2 (WTP3) in support of the WTP operations on the cesium-removal sorbent and supernatant, UOP IONSIV IE-911 CST from batch -0005 was used to treat the MVST supernatant from tank W-29 and was prepared for use in Building 4501 from the as-received CST. The loading was done at 12 CV/h (2-mL/min superficial velocity), and 13.3 L of W-29 supernatant was treated (the total received). The W-29 sample was prepared by mixing the two bottles of supernatant together five times to form a combined feed material.

The test was conducted at a flow rate of 12.58 CV/h in a 1.45-cm-ID column containing 18.15 mL of the CST with a bed depth of 11 cm. The W-29 feed was fed continuously to a 10.45% breakthrough point. The cesium-loaded column was removed from the cell and was sent to the ORNL Chemical and Analytical Sciences Division for TCLP testing. No problems were encountered during the operation of the column, and the results were again consistent with all previous results obtained using CST preparations. A total of 165.78 mCi ^{137}Cs was fed, with 160.4 mCi loaded. The amount of cesium loaded was equivalent to about 3842 Ci/m³ CST, below the 4600-Ci/m³ Class C limit, taking into account both columns of the two-columns-in-series operating plan. The sorbent from the loaded column was subjected to a modified TCLP procedure and showed that levels in the leach liquid were all below the regulatory limits.

1.1.2.8 CRC3 (WTP2) Qualification of CST and MVST W-31

In test CRC3 (WTP2), UOP IONSIV IE-911 CST from batch -0005 was used to treat the MVST supernatant from tank W-31 and was prepared for use in Building 4501 from the as-received CST. The loading was done at 12.7 CV/h (2-mL/min superficial velocity), and 9.75 L of W-31 supernatant was treated. The W-31 sample was prepared by mixing the two bottles of supernatant together five times to form a combined feed material.

The test was conducted at a flow rate of 12.69 CV/h in a 1.45-cm-ID column containing 17.07 mL of the CST with a bed depth of 10.4 cm. The W-31 feed was fed continuously to a 46% breakthrough point. The breakthrough curve is different from the CRC1 and CRC2 curves, with the breakthrough occurring much more rapidly, as expected for the higher-pH W-31 supernatant. The projected 50% breakthrough is 623 CV. The cesium-loaded column was removed from the cell and was sent to the ORNL Chemical and Analytical Sciences Division for TCLP testing. No problems were encountered during the operation of the column, and the results were again consistent with all previous results obtained using CST preparations. A total of 180.4 mCi ^{137}Cs was fed, with 147.4 mCi loaded. The amount of cesium loaded on the first column was equivalent to about 3755 Ci/m³ CST, below the 4600-Ci/m³ Class C limit, taking into account both columns of the two-columns-in-series operating plan. When the second column in the WTP system is operated as a guard column, the cesium in the supernatant that passes through the first column can be assumed to load on the second, as shown in the previous work. The total cesium fed can then be considered to load on the total CST in both columns, giving a total of 180.4 Ci loaded, equivalent to 4596 Ci/m³, just below the Class C limits. Assuming that 95% of the Class C limit is loaded, 4046 gal of W-31 supernatant can be passed through the system. The sorbent from the loaded column was subjected to a modified TCLP procedure and showed that all levels in the leach liquid were below the regulatory limits.

The results of the W-29, W-30, and W-31 tests were compared with the predictions from the model developed at Texas A&M for the K_d values from the batch tests, the cesium loading on the CST, and the predicted 50% breakthroughs from the column tests. Good agreement exists between the experimental and predicted K_d values for all three tests. There is also good agreement on the equilibrium loading on the CST for both supernatants between the batch tests and the model predictions. The 50% breakthrough values are 29% of the batch K_d for W-29 and 48% for W-30.

1.2 TESTING TWO CSTRS IN SERIES FOR THE SAVANNAH RIVER SMALL-TANK TPB PRECIPITATION SIMULATION (D. D. Lee, J. L. Collins, and C. W. Chase)

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Summary: One of the proposed methods of removing the cesium, strontium, and TRUs from the radioactive waste storage tanks at Savannah River is the small-tank tetraphenylborate (TPB) precipitation process. A continuously stirred tank reactor (CSTR) system (two reactors in series, each 15-L working volume) has been designed and construction begun to place the system in a hot cell to test the Savannah River-developed process. The system also includes two cross-flow filtration systems to concentrate and wash the slurry produced in the process, which contains the bulk of radioactivity from the supernatant processed through the system.

1.2.1 Purpose and Scope

This task describes the planned testing at ORNL to evaluate the decontamination achievable in the small-tank TPB precipitation process for the removal of cesium, strontium, and uranium from simulated Savannah River supernatant. It will also evaluate the catalytic decomposition of TPB during operation. The task is in support of the conceptual design phase for one of the selected alternatives to the High-Level Waste (HLW) Salt Disposition Project. As part of these tests, a CSTR system containing two CSTRs in series, each with a 15-L working volume, was designed. A precipitate concentration system (including a cross-flow filter), a precipitate wash system (with cross-flow filter), and various tanks and pumps to integrate the operations are included. Simulant supernatant, dilution water, recycle wash solution, sodium tetraphenylborate (NaTPB) solution, and monosodium titanate (MST) slurry will be fed to the first CSTR. Overflow from this CSTR will be passed into a second CSTR, which will then overflow to the third vessel, in which the slurry of precipitated potassium TPB, cesium TPB, excess NaTPB, sludge, and MST are concentrated. The filtrate from the slurry concentration step is the decontaminated product. The concentrated slurry will then be washed in a fourth vessel, and the washed solids will be stored as the HLW product. The wash solution will be recycled to the feed tank.

Information needed for the scaleup of the small-tank TPB precipitation process will be provided by these tests. Analyses to be performed during the operation of the process include high-performance liquid chromatography (HPLC) for K, Cs, Cu, B, Pd, Sr, and U to determine interstage conversion and demonstrate that the treated supernatant meets the required levels for WAC: Cs, <70 nCi/g; total alpha, <18 nCi/g; and Sr, <40 nCi/g. The desired levels of treatment—Cs, <40 nCi/g; alpha, <10 nCi/g; and Sr, <20 nCi/g—are set at ~50% of the WAC to allow for changes in process conditions. In this set of experiments, the alpha analyses will be

followed by analyzing uranium. The apparatus will be constructed of stainless steel with the CSTR vessels having a minimum of four inlet tubes. The CSTRs and other process vessels will be purged with nitrogen gas as required, and the CSTRs and filter feed vessels will contain a cooling coil to maintain $\pm 2^{\circ}\text{C}$ temperature control. The first test will be performed without the addition of the enhanced catalyst components, copper and palladium catalysts that have been shown to cause the decomposition of the TPB, but sludge surrogate supplied by Savannah River Laboratory will be added to the feed mixture. The precipitate washing system will not be used during the first test series; therefore, it will be performed with a simulated recycle stream. Test 1 will be divided into three phases (A, B, and C), with phases B and C to be conducted only if prior phases do not achieve the required DF. Phase A will use the excess TPB and residence time defined by previous Savannah River Technology Center tests and provided by the Savannah River Site (SRS). If the DF goals are not met, the amount of excess TPB will be increased (Phase B), and if the DFs are still not obtained, the residence time in Phase C will be increased to achieve the goal.

Test 2 will examine the fully integrated flow sheet, which includes measurements of several parameters (including interstage conversions of Cs, Sr, and U) and evaluation of the catalytic decomposition of TPB by copper and palladium catalysts. A minimum of four system turnovers (defined by four turnovers of the wash and concentrate tanks) will be performed for the test. The required residence times for CSTRs will be based on data from the test 1.

1.2.2 Progress

1.2.2.1 Equipment Design

The equipment will be installed in hot cell B in Building 4501 at ORNL. The small tank TPB precipitation pilot-scale system will use reactors with a 20-L total volume and a 15-L working volume. The CSTRs will be constructed from 316 stainless steel, with bottom drain/flush valves, and have flanged tops with center, flange-mounted agitators. The agitator size will be one-fourth the CSTR internal diameter. Each reactor will also include four baffles, which are one-twelfth the diameter of the tank and attached to the top flange. The vapor space of the CSTRs will be purged continuously with nitrogen gas during operation. The feed streams to the reactors will enter through the top flange and discharge under the surface of the liquid in the CSTR, near the agitator. The transfer lines from the reactors to the downstream vessel will also open at the liquid surface and exit through the side of the vessel. The supernatant mixture in the CSTRs will be internally cooled or heated by stainless steel cooling coils positioned below the working liquid level in the reactor. The coils will be attached to the top flange and will be removable to add versatility to the system.

The vessel for concentrating the precipitate will be the same size and configuration as the CSTRs, including the cooling coils. The working volume of the tank will vary as the amount of precipitate increases during the filtration. The contents of the tank will be pumped through a cross-flow filter using a progressive-cavity (Moyno) pump with 416 stainless steel chrome-plated rotor and an ethylene-propylene-diene monomer (EPDM) stator. The slurry will be returned to the vessel while the filtrate is being sent to the product collection tank. The supernatant filtered product will be tested for the required DFs while the precipitate is being concentrated to about 10% by weight solids. After accumulating the desired volume of 10% solids, the slurry will be transferred to the precipitate wash vessel. The wash vessel is similar to the precipitate concentration vessel but has a 7.5-L working volume (one-half that of the CSTRs). A second cross-flow filter is used to perform the precipitate washing step. The wash vessel is operated at constant volume with constant wash water feed and filtrate removal until the nitrite concentration is reduced to 0.01 M or less. The wash is used to remove excess salt and NaTPB for recycle to the system feed tank. The filtered wash liquid will be sent to the recycle storage tank, and the washed solids will be transferred to the solids storage tank. The solids wash cycle requires about 24 h.

Liquids and slurries will be transferred using small-volume gear and peristaltic pumps. Gear pumps will be used for the liquid feed streams to the first CSTR, and the peristaltic pumps will be used for intervessel slurry transfers. The 10% solids slurries in the precipitate concentrate tank and the precipitate wash tank will be transferred using the Moyno pumps normally used for the cross-flow filter feed.

The instrumentation and control strategy is currently being developed for the CSTR test system. Parameters that will be monitored and recorded include temperature, pressure, liquid level, density, pump speed, agitator speed, and flow rate. Feedback control systems will be used to control flow, level, and pressure. The control strategy for the process will be reviewed and approved by SRS and Oak Ridge personnel.

1.2.2.2 Materials

The MST, catalyst makeup, and sludge used in these tests will be supplied by SRS, and the supernatant simulants will be prepared at ORNL using a recipe provided by SRS. Normal cesium and strontium traced with ^{137}Cs and ^{85}Sr will be used to obtain the needed concentration of cesium and strontium in the simulated supernatant. In order to ensure the level of strontium added, the simulant will be treated with MST and then filtered to remove strontium impurities present in some

of the chemicals used to make up the feed. The amounts of tracers added will be dictated by the counting accuracy required after the TPB precipitation.

1.2.2.3 Test Description

CSTR sizes are 15,000-gal working volume. Assuming 20-L bench-scale vessels with 15-L working volume, scales are 1 gal = 1 mL and 1 gal/min = 1 mL/min. For the bench-scale system, the flow rates of the various feeds include the following:

Salt feed – 16.5 mL/min at 6.4 M Na⁺ and 0.017 M K⁺

Dilution water plus MST 0.4 g MST/L salt solution – 2.8 mL/min

Makeup NaTPB – 0.5 mL/min at 0.55 M TPB (stoichiometric; assumes no TPB decomposition)

Recycle wash water – 3.8 mL/min at 1.25 M Na⁺ and 0.03 M TPB – average (TPB is 50% excess)

Total flow exiting the CSTRs—23.6 mL/min of 0.5 wt % slurry; residence time in each CSTR—10.6 h

The operating process will make about 1.2 mL/min of 10 wt % unwashed slurry and 22.5 mL/min of decontaminated salt solution with about 4.7 M sodium. Experimental residence time for the CSTR for the first case is $t = 10.6$ h. For the first series, the tests are expected to last for 60 h (more than five residence times, or the time required for the production of one batch of precipitated concentrated solids) and make approximately 4 L of unwashed 10 wt % precipitate. Each part of the first test is expected to require the following volumes of feed and produce the following volumes of waste (all in liters):

Salt solution	60
Dilution water	10
Makeup NaTPB	1.8
MST slurry	0.2
Recycle wash water simulant (1.25 M sodium)	13.7
Decontaminated salt solution	81
10 wt % unwashed precipitate	4.3

The closed loop run will last about 264 h (about 11 days) and makes three batches of washed precipitate. The approximate volumes (in liters) for a 10.6-h residence time in the CSTR are as follows:

Salt solution feed	264
Dilution water	44
Makeup NaTPB	8
MST slurry	0.9
Wash water/recycle wash produced	$10.25 \times 4 = 41$

Decontaminated salt solution	356
10 wt % unwashed precipitate	$4.75 \times 4 = 19$
8.7 wt % washed precipitate	$4.83 \times 3 = 14.5$

The SRS has determined that the supernatant solution that will be used in the CSTR testing will be the average simulant. For operation of the CSTR during testing, the feed (6.4 M sodium), dilution water with MST slurry, TPB solution, and wash water recycle (1.25 M sodium) are added separately to CSTR 1 to operate at a 4.7 M sodium concentration in both CSTR 1 and CSTR 2.

2. PROCESS CHEMISTRY AND THERMODYNAMICS

E. C. Beahm

2.1 PREVENTION OF SOLIDS FORMATION (R. D. Hunt, E. C. Beahm, T. A. Dillow, and C. F. Weber)

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Summary: The FY 1999 test plan includes the following:

1. an evaluation of the formation of aluminosilicates during the caustic leaching of an actual sludge sample from a Hanford storage tank;
2. viscosity measurements of actual process waste solutions as a function of temperature;
3. tests with selected components to link their concentrations, temperatures, and viscosities (initial experimental design based on a two-level seven-factor partial factorial); and
4. tests in support of other TFA and user programs (primarily pipeline plugs).

A sludge sample from Hanford tank S-104 required five washes with inhibited water to remove essentially all of the water-soluble salts. Even though the wet solids weighed more than the original sludge sample, the progress of the water washes was successfully monitored using the ^{137}Cs activities in the used wash solutions. The washed solids were then leached with sodium hydroxide. In two of the ten leach tests, the dry weight of the sample increased during the leaching process. This result confirms the FY 1998 finding that solids can and do form during caustic leaching. A comparison of the caustic leach results with untreated and washed sludge from tank S-104 strongly indicated that a thorough water wash is needed prior to the caustic leaching. In addition, a procedure has been developed to plug a pipeline based on chemicals found in the Hanford tank waste. Finally, the experimental system for the viscosity measurements was assembled. The spindle, sample container, liquid volume, and test procedure were selected based on input from the manufacturer of the rheometer. Tests are under way to determine if these selections were appropriate.

2.1.1 Purpose and Scope

Nuclear waste remediation efforts at Hanford and Savannah River have been adversely affected by unwanted or unintentional solids formation. Transfer pipes at Hanford and Savannah

River have become plugged with the nuclear waste, leading to schedule delays and to higher remediation costs. Fortunately, operating windows where solids can form during tank operations such as pretreatment, transfers, and storage can be predicted. These windows are based on thermodynamic calculations that use ionic strengths and the concentrations of phosphate, fluoride, silica, alumina, and hydroxide. To improve process control, it will also be necessary to correlate chemical effects and solid formation with physical properties, which can be continuously monitored if necessary. The properties of interest in many operations are viscosity and specific gravity. The ultimate aim is to provide relationships between the chemistry and physical properties so the tank farm operators can avoid unwanted or unintentional solids formation.

2.1.2 Progress

At the request of the TFA, a test plan for the FY 1999 research effort was submitted to the Pretreatment Technical Integration Manager. The approved test plan consists of the following research activities:

1. an evaluation of the formation of aluminosilicates during the caustic leaching of an actual sludge sample from a Hanford storage tank;
2. viscosity measurements of actual process waste solutions as a function of temperature;
3. tests with selected components to link their concentrations, temperatures, and viscosities (initial experimental design based on a two-level seven-factor partial factorial); and
4. tests in support of other TFA and user programs (primarily pipeline plugs).

2.1.2.1 Formation of Aluminosilicates

A 40.34-g sample of sludge from Hanford tank S-104 required five washes with inhibited water to remove essentially all of the water-soluble salts, which weighed 18.73 g. Even though the wet solids weighed 27.5% more than the original sludge sample, the progress of the water washes was successfully monitored using the ^{137}Cs activities in the used wash solutions. The slow weight gains indicated that the initial sludge sample was dehydrated, and the rehydration process in a tank with a dehydrated sludge and limited mixing capabilities can be very slow.

The washed solids were then leached with sodium hydroxide using some of the same conditions that were used in the FY 1998 parametric Enhanced Sludge Washing study on sludge from tank S-101 and in the FY 1997 tests on sludge from tank S-101. In two of the ten leach tests, the dry weight of the sample increased during the leaching process. Since the dry weight gain of 16.9% for one of the samples greatly exceeds the experimental uncertainties, this result confirms the

FY 1998 finding that solids can and do form during caustic leaching. An analysis of available analytical data indicated that most of the newly generated solids are probably sodium aluminosilicates.

A comparison of the caustic leach results with untreated and washed sludge from tank S-104 strongly indicated that a thorough water wash is needed prior to the caustic leach. The presence of water-soluble salts in the caustic leach solution increases the ionic strength on the solutions. Ionic strength has a direct impact on the solubilities of Al, phosphate, Si, and Na. The change in solubilities can increase the rate of solids formation, and the presence of nitrate can alter the chemical composition of the solids. Finally, it appears that the presence of water-soluble salts can produce large differences in the effectiveness of the caustic leaches when only small changes are made in the process conditions.

2.1.2.2 Pipeline Plugs

A procedure has been developed to plug a pipeline based on chemicals found in the Hanford tank waste. This formulation for a chemical plug was sent to the coordinators of a university contest on methods to unplug a plugged transfer line. The procedure has been used to plug pipes in Oak Ridge and in New Mexico, which is the site of the contest. University students in New Mexico are currently developing methods to remove the chemical plug. These methods will be judged by university and TFA personnel in April.

2.1.2.3 Viscosity Measurements

The experimental system for the viscosity measurements was assembled. The system includes a Brookfield rheometer and a water bath for temperature control. A technical representative from Brookfield was contacted in an effort to determine the best spindle for our objectives. Input from the Brookfield representative was used to select the spindle, sample container, liquid volume, and test procedure. Tests are under way to determine if these selections were appropriate.

2.1.3 Publication

A. Singhal, G. Skandan, A. Wang, N. Glumac, B. H. Kear, and R. D. Hunt, "On Nanoparticle Aggregation During Vapor Phase Synthesis," *Nanostructured Materials* (1999), submitted.

2.2 SALTCAKE DISSOLUTION (E. C. Beahm)

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Summary: Comparison calculations of a chemical system important to solid formation showed that the Environmental Simulation Program (ESP) and the SOLGAS routine gave somewhat different results when one mode of the ESP was used and similar results when another mode was employed. These differences, based on calculational options in ESP, warrant further evaluation because of the reliance on ESP for waste handling at Hanford.

2.2.1 Purpose and Scope

This effort provides coordination and thermochemical evaluations for a team effort on Hanford saltcake dissolution. Tests on Hanford saltcake are run at Numatec Hanford, and calculations using the ESP are being run at Mississippi State University. Some of the key issues that are being addressed include the solution conditions required to dissolve saltcake and validation of the ESP code.

2.2.2 Progress

Because of the reliance on the use of the ESP to produce accurate models of waste handling and treatment at Hanford, it is important to evaluate it by comparison with another computer routine and with assessed data. The SOLGAS routine is the computer code that is being used in this comparison. The comparison calculations are being done on the Na-F-PO₄-HPO₄-OH system. This system was selected because of its potential to form troublesome solids during waste handling.

Calculations in this series of comparisons of ESP and SOLGAS results showed that at low sodium hydroxide concentrations, the solubility of sodium fluoride phosphate in the ESP results was equal to or greater than the maximum concentrations from the SOLGAS data assessment. However, at high sodium hydroxide concentrations, the opposite was true and the ESP results were lower than the lower assessed values. As thermodynamic values from SOLGAS were being inserted into ESP, it was noted that the ESP code bases its calculations either on fitted solubility data or on free energy values. The results that were calculated were based on fittings of solubility data. When free energy was used instead, the solubility of sodium fluoride calculated by ESP and SOLGAS was very similar. Further evaluation of the different modes of calculating the same equilibria in ESP is warranted.

3. MSRE REMEDIATION STUDIES

D. F. Williams

3.1 URANIUM CONVERSION (G. D. Del Cul, A. S. Icenhour, D. W. Simmons, and J. Caja)

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Summary: Fissile ^{233}U is presently being recovered, trapped, and removed as an essential part of the remediation and decommissioning activities presently under way at the Molten Salt Reactor Experiment (MSRE). Uranium hexafluoride trapped in NaF, along with uranium-laden activated charcoal, represents the bulk of the inventory. For permanent storage, all of the ^{233}U needs to be recovered and transformed into a stable oxide. Efforts focused on prototypical conversion of the UF_6 sorbed on NaF, preparation of uranium-laden passivated charcoal [auxiliary charcoal bed (ACB) simulant] for future conversion trials, preparation of the Building 4501 facility for conversion operations, and assembly and identification of the cold-test mock apparatus. The conversion facility is scheduled to start the actual conversion operation in August 2000.

3.1.1 Purpose and Scope

The MSRE at Oak Ridge has been shut down since 1969, when the fuel salt was drained from the core into two drain tanks at the reactor site. In January 1994, analytical measurements of gas samples taken from the gas piping circuitry connected with the drain tanks indicated the presence of fluorine, 350 mm Hg, and uranium hexafluoride, 70 mm Hg. Although radiolysis was known to generate F_2 , the formation of UF_6 and its transport from the fuel salt were unexpected. Additional investigation confirmed the belief that these gaseous products had moved through the piping to a charcoal bed. After these findings, a multiyear project was launched to remediate the potentially hazardous conditions generated by the movement of fissile material and reactive gases.

The extensive remediation and clean-up activities related to the MSRE involve (1) the trapping of the gaseous products; (2) deactivation, removal, and recovery from the activated-charcoal bed; (3) stabilization and reconditioning of the fuel salt; (4) recovery of ^{233}U ; and (5) conversion of ^{233}U compounds into a stable oxide for final safe storage and disposition. One of the essential tasks is the recovery and conversion of all of the ^{233}U materials into a stable oxide for permanent storage.

3.1.2 Progress

Preparation of the passivated uranium-laden charcoal was completed. The material was loaded into a reaction vessel and attached to the conversion prototype in Laboratory 123 of Building 4501. Full-scale testing of uranium-laden charcoal processing was initiated. The 90%

design of the conversion process was completed. The final process will first be installed in the Building 4501 high bay and cold tested prior to installation in hot cell D. Mockup hot cell walls have been installed in the high bay, and fabrication of the in-cell table frame was initiated. The manipulator mockup located in the Building 4501 high bay was used to test special tools required for use in the hot cell. The air-lock entrance to the facility was completed by the installation of a second set of doors. Unnecessary equipment and piping on top of hot cell D were removed. Comments from the initial review of the safety analysis report and the technical safety requirements document for Building 4501 are being resolved. After completion of comment resolution, these documents will be reviewed by the Laboratory Facility Authorization Basis Board. Nuclear criticality safety reviews are continuing.

3.2 RADIOLYSIS AND MATERIALS DISPOSITION STUDIES (D. F. Williams, A. S. Icenhour, L. D. Trowbridge, L. M. Toth, and J. Brynstad)

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Summary: Hydrofluorination of the first large batch of irradiated MSRE fuel salt simulant was completed. Initial observations and results indicate that restoration of fluorine to the salt was successful. Additional data from the uranium-loaded NaF traps at Building 3019 indicate that the buildup of pressure is steady and predictable and in the range expected. New samples of uranium oxide and uranium oxyfluoride samples were prepared, and ^{60}Co irradiation of this new series was begun.

3.2.1 Purpose and Scope

Understanding the radiolysis of MSRE fuel salt, uranium oxides, and other materials that derive from conversion of the recovered UF_6 is necessary in order to proceed with remediation, interim storage, and permitted storage of the radioactive MSRE materials. The most significant remediation activities for the MSRE include (1) removal and recovery of uranium from the off-gas system, (2) removal of the uranium-laden charcoal from the charcoal bed, and (3) removal of the stored fuel salt. These retrievable intermediate materials are not suitable for long-term storage and must be converted to a more stable form. In the case of the MSRE fuel salt, it is also necessary to understand the chemical consequences of the radiolysis in order to safely melt and treat the salt. A recent addition to the scope of this work has included short-term tests and analyses to support the interim storage of materials before they are converted into stable oxides.

3.2.2 Progress

The first large batch (~800 g) irradiated at the High Flux Isotope Reactor (HFIR) was melted and hydrofluorinated in February. The salt was placed in a furnace, melted, and then sparged with HF. When first melted, the salt was very dark and opaque, with some indications of nonliquid material in the melt. As sparging progressed, the salt became more transparent, and a red color was observed. Utilization of HF fell as the sparge proceeded and clarity of the salt improved, although consumption of HF appeared to rise again late in the treatment. Agreement was achieved between the amount of HF consumed [as determined both by exhaust titration and Fourier transform infrared (FTIR) gas analysis] and the amount demanded by the salt. When allowed to freeze, the salt showed the light green color indicative of UF_4 and a reconditioned salt. The results of this test are very encouraging; further testing will address the changes in HF utilization late in the campaign. A second large batch of simulated fuel salt was prepared and loaded into the HFIR cooling pool for irradiation. A second hydrofluorination test will probably be required to investigate the unaccounted-for HF behavior late in the experiment.

Two UF_6 -laden NaF traps in storage at Building 3019 are instrumented to monitor pressure buildup (i.e. production of F_2 by radiolysis). Sufficient history has been accumulated on the two traps to reveal that their pressure buildup is very similar on the basis of quantity of F_2 produced per radiation dose. Some variation in pressure is apparent in response to seasonal temperature variations. The rate of rise, however, is approximately linear in time for both traps. The overall behavior of the two traps is sufficiently regular that it should be possible to predict the pressure buildup of the noninstrumented traps with some degree of confidence.

Radiolysis studies were conducted in support of the development of the ^{233}U storage standard. Two uranium oxide samples with sorbed water were placed in the ^{60}Co irradiator— $\text{UO}_3 \cdot x\text{H}_2\text{O}$ (5.6 g, 1.7 wt % H_2O) and U_3O_8 (7.1 g, 0.7 wt % H_2O). The purpose of these experiments is to evaluate the potential pressure increase from the radiolysis of residual water on uranium oxides. Additionally, two UO_2F_2 samples were placed in the ^{60}Co irradiator— UO_2F_2 (7.5 g) and $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$ (10.3 g). Earlier experiments with these types of uranium oxyfluorides have resulted in the production of CO_2 and O_2 , with no F_2 or HF production observed. It appears that the CO_2 results from the reaction of oxygen radicals with carbon impurities in the samples. Pressure in the sample containers for the four experiments will be monitored. The samples will be removed from the irradiator during the next quarter, and gas samples will be withdrawn for analysis.

During an operation in late December designed to explore the character of the uranium-laden charcoal in the ACB at MSRE, a brief gas pressurization and release (confined by secondary

containment) occurred. In January, Chemical and Energy Research Section personnel investigated possible causes of the gas release. The investigation concluded that the most probable cause was reaction of low-concentration radiolytically regenerated carbon fluoride with NH_4F . The NH_4F was produced in the ACB during the February 1998 "denaturing" activity, in which the suspected much-higher-concentration carbon fluorides were reacted with anhydrous ammonia to prevent a potentially much more severe decomposition of the carbon fluoride. Carbon fluoride is likely regenerated by the slow radiolysis of fluorine-containing compounds (UF_4 , NH_4F). The triggering event apparently was the insertion of a hot drill bit into a region containing NH_4F , which sublimates to gaseous HF and NH_3 , allowing rapid spread of the reaction to adjacent areas.

4. CHEMISTRY RESEARCH

D. F. Williams

4.1 MOLECULAR IMPRINTING ON SOL-GEL MATRICES (S. Dai, Y. H. Ju, M. C. Burleigh, S. D. Waezsada, and C. C. Morrow)

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Summary: A new method has been developed to effectively functionalize surfaces of mesoporous materials prepared by cationic surfactants through the use of the ion-exchange reaction between cationic surfactant molecules and cationic coating complexes. Metal ions serve as a "catalyst" in this functionalization method. This has led to a simplified experimental procedure for functionalizing mesoporous materials.

4.1.1 Purpose and Scope

The purpose of this research is to incorporate molecular recognition in advanced sorbent development. The design principles illustrated by these results highlight opportunities for application of imprint-coated mesoporous materials in areas such as selective sorption, chemical sensing, and catalysis.

4.1.2 Progress

In many applications of mesoporous materials, functionalization of silanol surfaces is required. Presently, extensive research is being conducted to develop procedures to introduce silane ligands into the surfaces of the ordered mesoporous materials. The generally accepted mechanism for direct coating involves the initial hydrolysis of siloxane groups in the silane ligand followed by condensation with the surface silanol groups to produce ligands that are covalently bound or

"tethered" to the surfaces. Drawbacks associated with this direct coating method are (1) the requirement for time-consuming reflux syntheses (>24 h) and (2) the low loading of functional silane ligands. These drawbacks led us to develop a new and more efficient method for functionalizing surfaces of ordered mesoporous materials that not only simplifies the experimental procedure but also increases the loading of the ligand on pore surfaces. The success of our new functionalization method relies on the ion-exchange reaction. Accordingly, we call this new coating method ion-exchange functionalization.

The ion-exchange reaction has been extensively used to prepare novel intercalate materials. The general reaction mechanism can be expressed as follows:

where (S-O⁻) is a surface anionic group in inorganic materials such as the galleries of pillared materials; M₁⁺ is a singly charged cation in as-synthesized materials; and M₂^{m+} is a new cationic species targeted for intercalation into these materials. Ordered mesoporous materials synthesized by the use of cationic surfactants have the same structural features as those of ionic intercalate materials. In this case, the (S-O⁻) groups correspond to the SiO⁻ anions on the mesopore surface, while M₁⁺ is a cationic surfactant ion. The cationic surfactant ions are organized in the form of a cylindrical micellar structure with hydrophilic positive ends interacting with the charged silica pore surfaces. The weak coulombic interaction can be easily broken or replaced by another cation through ion exchange.

Two ionic complexes used to demonstrate the ion-exchange coating are Cu(aapts)₂²⁺ and UO₂(aapts)₂²⁺. They were prepared by methods similar to those described in the literature. The two solvents used in our cation-exchange coating were ethanol (EtOH) and dimethyl sulfoxide (DMSO). Removal of the Cu²⁺ or UO₂²⁺ cation to produce functionalized mesoporous MCM-41 materials was accomplished by protonating amine groups in s-aapts with a 1 N nitric acid wash solution. The wash solutions were collected in volumetric flasks. The concentration of Cu²⁺ and uranyl ions in these wash solutions can be determined using inductively coupled plasma-atomic emission (ICP-AE) and spectrophotometric analyses, respectively. The spectrophotometric analysis of the uranyl concentration was conducted using Arsenazo III as an indicator reagent. The loading of the bifunctional ligand on these mesoporous sorbents can be estimated from the metal-ion concentrations in the wash solutions, assuming that each metal ion complexes with two equivalents of the bifunctional ligands. These estimates were compared with the loadings of the bifunctional ligand, which were determined

directly from ICP-AE analysis of the carbon content of the solutions from HF digestion of the corresponding imprinted ordered mesoporous sorbents.

4.2 IONIC LIQUIDS RESEARCH (S. Dai and Y. H. Ju)

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Summary: Thermodynamic analysis of the ion-pair dissolution processes led us to develop a novel solvent-extraction process based on room-temperature molten salts in conjunction with macrocyclic ligands. Four additional room-temperature ionic liquids were synthesized using modified metathesis reactions.

4.2.1 Purpose and Scope

The purpose of this research is to conduct a spectroscopic investigation into the fundamental interaction between ionic solvents and solutes in both low-temperature and high-temperature ionic liquids (e.g., molten salts). The fundamental knowledge gained in these studies will be used to design novel separation systems involving ionic liquids.

4.2.2 Progress

The solvent properties of these ionic liquids may be systematically influenced by both the size and position of the alkyl substituents on the organic cations and also by the nature of the associated anions. The room-temperature molten salts synthesized have the following general structural form:

where R_1 = ethyl, propyl, or butyl and R_2 = H, or methyl, and 1- R_1 -2- R_2 -3- methylimidazolium hexafluorophosphate ($\text{R}_1\text{R}_2\text{MeIm}^+ \text{PF}_6^-$). These molten salts are *immiscible with water*. The chemical formula were confirmed by nuclear magnetic resonance (NMR) and elemental analysis.

4.3 INVITED CONFERENCES

S. Dai, "Molecular Recognition in Ionic Media," Symposium on Heavy Element Complexes: The Convergence of Theory and Experiment, 217th American Chemical Society National Meeting, Anaheim, California, March 21-25, 1999.

- S. Dai, "Imprinting Coating: Novel Synthesis of Selective Functionalized Ordered Mesoporous Sorbents," Inorganic Materials for Separation, 217th American Chemical Society National Meeting, Anaheim, California, March 21-25, 1999.
- L. D. Trowbridge, G. D. Del Cul, D. W. Simmons, D. F. Williams, and L. M. Toth, "Passivation of Fluorinated Activated Charcoal," American Chemical Society Fourteenth Winter Fluorine Conference, St. Petersburg, Florida, January 17-22, 1999.
- A. S. Icenhour, L. M. Toth, L. D. Trowbridge, G. D. Del Cul, D. F. Williams, and D. W. Simmons, "Radiolysis Studies of Fluorine-Containing Compounds for the Remediation of the Molten Salt Reactor Experiment," American Chemical Society Fourteenth Winter Fluorine Conference, St. Petersburg, Florida, January 17-22, 1999.
- G. D. Del Cul, L. D. Trowbridge, D. W. Simmons, and D. F. Williams, "Investigations on the Chemistry of Activated Charcoal with Uranium Hexafluoride and Fluorine," American Chemical Society Fourteenth Winter Fluorine Conference, St. Petersburg, Florida, January 17-22, 1999.

4.4 PUBLICATION

- L. D. Trowbridge, *Potential Hazards Relating to Pyrolysis of $c\text{-C}_4\text{F}_8$ in Selected Gaseous Diffusion Plant Operations*, ORNL/TM-13758, March 1999.

5. SEPARATIONS AND MATERIALS SYNTHESIS

D. W. DePaoli

5.1 CHEMICAL AND PHYSICAL PRINCIPLES IN MULTIPHASE SEPARATIONS (D. W. DePaoli, C. Tsouris, D. D. Bruns, B. A. Grant, and S. U. Sarnobat)

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Summary: Fundamental studies of multiphase systems, particularly those that explore the use of electromagnetic fields to enhance transport processes, are continuing. Progress has been made in several areas, including: (1) spraying and mixing in electrohydrodynamic (EHD) flows and (2) particle interactions under magnetic fields and in reactive systems.

5.1.1 Purpose and Scope

This program, funded by the DOE Office of Basic Energy Sciences, comprises several fundamental studies that explore transport processes in multiphase separations, with particular emphasis placed on the application of electromagnetic fields for enhancement. Experimental, theoretical, and computational methods are employed to investigate the effect of electromagnetic fields on transport processes in liquid-liquid, gas-liquid, and solid-liquid systems. This work will

provide information necessary to devise novel means to dramatically improve transport rates in these systems and, thus, will have widespread benefit for separations processes such as solvent extraction and distillation as well as applications in environmental and biotechnology areas. The areas of current focus are (1) enhancement of transport processes through EHD flows and (2) interactions and coalescence/aggregation of particles and drops.

5.1.2 Progress

Technical progress was made in several areas, as described briefly in Sects. 5.1.2.1–5.1.2.5. In addition, we have recruited a new staff member to work on this project. Valmor F. de Almeida, who will start work at ORNL in April 1999, has expertise in fluid dynamics and parallel computing.

5.1.2.1 EHD Spraying

A dimensional-analysis approach was employed to determine the parameters, including physical properties and operating conditions, responsible for pumping and spraying phenomena caused by EHD flows. Based on scaling arguments and experimental data using a phase-Doppler velocimeter, a relationship of the flow velocity with physical properties, geometry, and operating conditions was derived. A paper is in preparation.

5.1.2.2 Nonlinear Bubble Production

Studies of the dynamics of drop/bubble formation by inverse electrostatic spraying have been conducted in collaboration with Professor D. D. Bruns of The University of Tennessee. Experiments involving spraying of a gas at constant flow rate into a liquid through an electrified nozzle have shown that bubble-formation dynamics exhibit the classic signs of a period-doubling bifurcation to chaos with increasing applied potential. The behavior is similar to that of the classic dripping faucet and of bubble formation in liquids under increasing flow rate. This discovery has several important implications: (1) richer dynamic behavior is possible for the electrified system, (2) an exploration of the different operating regimes is necessary to employ inverse spraying for production of monodispersed droplets/bubbles, and (3) it may be possible to employ electrical pulsing for control of drop/bubble production.

5.1.2.3 EHD Mixing

Recent combined efforts with the program "Nucleation, Growth, and Transport Phenomena" (see Sect. 5.2) have focused on utilizing EHD flows for mixing. This work has led to two useful discoveries: (1) EHD flows provide the capability for rapid mixing at microscopic scales, and (2) electrodispersion of miscible reactive fluids provides an efficient new approach to inorganic

particle production. This has been demonstrated by the production of homogeneous submicron particles by sol-gel reactions under fast reaction conditions for which conventional sol-gel processing yields undesirable products.

5.1.2.4 Particle Interactions Under Magnetic Fields

Modeling and experimental studies on the aggregation of colloidal magnetic particles were continued. Modeling included a trajectory analysis incorporating particle-particle interactions and particle-field interactions. An important finding is that the main mechanism of aggregation is Brownian diffusion rather than differential sedimentation; this result underscores the need to employ Brownian dynamics in future simulations to better describe the kinetics of formation and structure of chains of magnetic particles. Based on modeling and experimental results, a paper entitled "Diffusional Coagulation of Superparamagnetic Particles in the Presence of an External Magnetic Field" was submitted for publication in *Physica A*. The formation of magnetite by an electrochemical method was investigated, and a paper entitled "Electrocoagulation for Magnetic Seeding of Colloidal Particles" was submitted for publication in *Colloids and Surfaces*.

5.1.2.5 Particle Interactions in Reactive Systems

The behavior of colloidal sorbent silica and iron oxide particles in copper and cadmium solutions has been experimentally investigated in collaboration with Professor S. Yiacoymi. The objective was to observe surface-charge modifications during sorption and their effect on aggregation kinetics of sorbent particles. A large increase in the zeta potential of the particles was observed during sorption of metal ions; similar results were observed in precipitation experiments of copper ions. Based on these results, a paper entitled "Sorption of Copper by Inorganic Particles—Equilibrium, Kinetics, and Particle Interactions: Experimental" was prepared and submitted for publication in *Colloids and Surfaces*.

5.2 NUCLEATION, GROWTH, AND TRANSPORT PHENOMENA (M. Z.-C. Hu, C. H. Byers, K. R. Booth, B. A. Grant, V. Kurian, and D. E. Newton)

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Summary: This project aims to develop understanding of nucleation and growth of clusters/particles involved in homogeneous or heterogeneous systems. A new synthesis route for nanocrystalline barium titanate microspheres was successfully developed by combining dielectric tuning solution synthesis with the low-temperature hydrothermal conversion. We discovered a novel thin-film deposition phenomenon (via molecular design and nanocluster docking).

5.2.1 Purpose and Scope

This research program, funded by the Office of Basic Energy Sciences, involves materials chemistry and synthesis and fundamental studies of nucleation and growth phenomena in chemically reactive systems for synthesis of ultrafine (particularly nanosized), monodispersed particles (i.e., oxide ceramic precursor powders) and for solution deposition of ceramic films. A primary goal is the understanding of the mechanisms, kinetics, and thermodynamics of nucleation and particle growth under controlled sol-gel and wet-chemical processing conditions.

Our current emphasis in nanoscale/nanostructured materials lies with the chemistry, reaction engineering, colloidal/interfacial science, and materials science involved with three major wet-chemical systems: (1) homogeneous precipitation of nanospheres and microspheres in inorganic salt solutions of mixed solvent; (2) hydrothermal processing of inorganic salt aqueous solutions; (3) acid- or base-catalyzed hydrolysis and condensation of organometallic compounds (such as alkoxides) in water-alcohol solutions; and (4) ceramic film deposition onto self-assembled monolayers (SAMs) in solutions. Experiments utilize several specially developed techniques, including real-time dynamic light scattering (DLS), rapid-mixing flow cell coupled with FTIR and small-angle X-ray scattering (SAXS), as well as high-temperature X-ray diffraction (XRD), electron microscopy, Raman spectroscopy, and electrostatic spraying.

It is anticipated that the results of this work will have significant impacts upon development of advanced materials such as nanoscale and nanophase ceramics that have dramatically improved properties over traditional "coarse-grained" ceramics. These advanced ceramics are potential candidates as structural ceramics, electroceramics, catalysts, nanocrystalline thin films, coatings, and nanostructured inorganic membranes.

5.2.2 Progress

5.2.2.1 Hydrothermal Processing

A low-temperature hydrothermal reaction scheme has been developed to produce pure, ultrafine, uniform-sized, nanocrystalline barium titanate (BaTiO_3) microspheres from two inorganic precursors: synthesized titania microspheres and barium hydroxide solutions. The size and morphology of titania (TiO_2) microspheres were controlled by tuning the dielectric constant of the mixed-solvent system. Monodispersed barium titanate microspheres approximately $0.1\text{--}1\text{ }\mu\text{m}$ in diameter were successfully synthesized from titania via a hydrothermal reaction ($\leq 100^\circ\text{C}$) in barium hydroxide solutions. The microspheres were characterized by scanning electron microscopy and room-temperature XRD. High-temperature XRD was also utilized for in situ study of the phase

transformations and changes of crystallite size with calcination temperatures. The size and morphology of the barium titanate particles remained the same as the precursor titania particles, indicating a "shrinking-core" diffusion-reaction mechanism. The as-prepared barium titanate was in the cubic nanocrystalline form and did not change when the temperature was held at levels as high as 750°C for over 5 h.

5.2.2.2 Fabricating Thin Films by Nanocluster Docking

Nanostructured materials have been called "magical" materials because of their dramatically improved properties (mechanical, electrical, optical, etc.) relative to those of conventionally produced materials. The major obstacle to application of these innovative materials lies in developing ways to controllably construct items from them. Because the building blocks for nanostructured materials are smaller than 100 nm, radically new techniques must be used to grow and arrange them.

We have uncovered a simple, low-temperature approach to production of nanostructured films. This approach involves adjustment of the chemistry of a solution in which reactions take place to form nanoclusters (the building blocks). When this solution is in contact with a solid surface such as a silicon wafer, interactions occur between the nanoclusters and the solid surface. With proper molecular design, the nanoclusters recognize a surface and "dock" directly to it, creating uniform, ultrathin films—even on the most complex of surface shapes. Furthermore, multilayer films are easily achieved by this technique, opening new frontiers in the area of the coating of optical communications. This molecular-directed approach has been successful in fabricating high-quality optical thin films on silicon wafers. These films could provide a possible breakthrough in enhancing computer performance through use as nanowaveguides for on-chip, high-speed optical interconnections.

5.2.2.3 Outside Interactions

A new research collaboration was initiated with Dr. Thomas Niesen at the Max-Planck Institute, Stuttgart, Germany, on studies of ceramic thin-film deposition on SAMs. Michael Z.-C. Hu recently presented a lecture, "Chemical, Biomimetic/Biomolecular Fabrication of Nanoscale and Nanostructured Materials," at the Naval Research Laboratory (Center for Bio/Molecular Science and Engineering).

5.3 PHASE EQUILIBRIA MODIFICATION BY ELECTRIC FIELDS (C. Tsouris, K. D. Blankenship, D. W. DePaoli, and J. Dong)

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Summary: Fundamental studies are being undertaken that explore the use of electric fields to modify phase equilibria in multiphase separations processes. Experimental systems have been assembled and are currently used to investigate transport and thermodynamic effects of electric fields on vapor-liquid and liquid-liquid systems. Batch-distillation, vapor-liquid-equilibria, liquid-liquid-equilibria, and solid-liquid-equilibria experiments are in progress, using various liquid mixtures of polar-nonpolar, polar-polar, and nonpolar-nonpolar components. The results obtained to date show that electric fields have an effect on the vapor-liquid and solid-liquid equilibria of some systems.

5.3.1 Purpose and Scope

The primary objective of this project, funded by the Environmental Management Science Program (EMSP), is to enhance separations of mixtures by applying an electric field across an interface between two phases. Enhancement in separation may be achieved either by increasing transport rates through the interface or by changing the phase equilibria. Electric fields have been known to interact with charge carriers, such as ions and electrons, leading to higher mass and heat transfer rates, fluid atomization, mixing, and pumping, which are transport effects. The effects of electric fields on the behavior of noncharged molecules and ions and the macroscopic thermodynamic behavior of the system are examined in this project.

5.3.2 Progress

Experiments to determine the effect of an applied electric field on vapor-liquid separations were continued. A small, but significant, effect is seen when an electric field is applied across the vapor-liquid interface of polar-nonpolar and polar-polar mixtures. The results suggest a mechanism stemming from charge buildup at the interface. Kevin D. Blankenship successfully completed his M.S. thesis on this work.

Liquid-liquid experiments were continued using a two-phase system consisting of water, toluene, and isopropanol. The two phases were introduced in a specially designed cell equipped with two electrodes. An electric field was applied across the interface of the two phases with the objective of observing changes in the equilibrium concentration of each phase. Liquid bridges of the aqueous phase were formed, extended from the interface in the organic phase. The formation of these bridges was investigated as a function of applied voltage and concentration of the three

species. Additional experiments were conducted in which a stirred tank was used to form a liquid-liquid dispersion and an electric field then applied to manipulate the dispersed and continuous phases. The effect of an electric field on the ambivalence region (i.e., the region in which either phase may be continuous or dispersed) was also investigated. It was found that the ambivalence region is strongly modified by the electric field to the point that, by turning the field on and off, one may invert the phases back and forth.

Solid-liquid-equilibria, or electrosorption, experiments were also continued to investigate the effect of electric fields on the separation of ions from aqueous solutions. A new reactor with carbon aerogel was constructed, and additional equipment was installed to provide on-line data concerning solution pH, conductivity, and concentration of metal ions. One reactor is currently used for equilibrium studies, and another is used for kinetic studies, both with and without an applied electric field. Modeling studies were also initiated in collaboration with investigators at Georgia Institute of Technology.

5.4 ELECTROSTATIC OZONATION (C. Tsouris, D. W. DePaoli, S. Yiacoumi, and W.-T. Shin)

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Summary: Electric fields are used to form microbubbles containing ozone for the oxidation of organic pollutants in aqueous solutions. An experimental apparatus has been set up for (1) ozone generation from air or oxygen by means of corona discharge; (2) ozone spraying in an aqueous phase containing an organic solute, such as phenol, by inverse electrostatic spraying; and (3) collection of gas and liquid samples for chemical analysis. Experimental results showed an enhancement in the oxidation rate by electrostatically generated microbubbles, as compared with conventional bubble diffusers.

5.4.1 Purpose and Scope

The primary objective of this project, funded by the Electric Power Research Institute (EPRI), is to enhance the efficiency of ozonation processes by inverse electrostatic spraying. Ozone is a strong oxidant of organic molecules with fast reaction kinetics; thus, in most cases, ozonation is a mass-transfer-limited process that can be improved by decreasing the size of ozone-containing gas bubbles. Introduction of ozone in the form of microbubbles enhances the oxidation efficiency by (1) increasing the surface area per unit volume between the gas and liquid phases and (2) increasing the gas volume fraction (since smaller bubbles have a lower rise velocity than larger bubbles). This project is aimed at applying the knowledge gained in our fundamental studies of

inverse electrostatic spraying to develop an efficient means for production of ozone-containing microbubbles.

5.4.2 Progress

Experiments including (1) mass-transfer of ozone from the bubbles to deionized water, (2) oxidation of methylene blue dissolved into water, and (3) oxidation of phenol were conducted. Results showed that if oxygen is used under corona-discharge conditions, instead of ozone, a similar oxidation rate of phenol and methylene blue is observed, which indicates that the need for ozone may be eliminated. Modeling studies of phenol oxidation under corona discharge have been initiated.

5.5 ELECTRODISTILLATION (C. Tsouris, D. W. DePaoli, and K. D. Blankenship)

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Summary: The enhancement of distillation efficiency by using electric fields is investigated in this task. A three-stage distillation column and a one-stage column with coaxial electrode configuration have been designed and constructed, which allow high-intensity electric fields to be formed across the interface of liquid and vapor phases. Experiments were conducted to determine whether electric fields could be used to enhance the separation efficiency of binary mixtures.

5.5.1 Purpose and Scope

The primary objective of this project, funded by EPRI, is to enhance the separation factor of distillation of liquid mixtures by using electric fields. Transport effects on pumping, spraying, and mixing of bubbles in the liquid, as well as equilibria effects, have the potential to enhance separation by distillation. These expectations are supported by earlier work on phase equilibria modification by electric fields, batch distillation, and EHD experiments using gas-liquid systems.

5.5.2 Progress

Experiments conducted as part of this project were completed, and a report was submitted to EPRI. It was concluded that electric fields can be used to enhance the distillation efficiency by mass-transport effects. The enhancement in the separation factor of the mixtures used in this study, however, was limited to less than 5%.

5.6 OZONE TREATMENT OF SOLUBLE ORGANICS IN PRODUCED WATER (D. W. DePaoli, K. T. Klasson, C. Tsouris, and A. B. Walker)

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Summary: Complete destruction of the water-soluble organics benzene, toluene, ethylbenzene, and xylenes (BTEX) as well as aliphatic acids has been obtained in laboratory-scale experiments conducted with ozone and ultraviolet induction in artificial seawater. Near-complete destruction of aromatics has been obtained with a sonochemical system that generates hydrogen peroxide in the produced water. Destruction of hexane-extractable materials using ozone was achieved in 5 min in a water stream very similar to produced water. Studies have shown that sharp improvement in the effectiveness of ozonation is closely linked to the generation of small bubbles. These laboratory results are guiding the next phase of study.

5.6.1 Purpose and Scope

Oil production is shifting from "shallow" wells (0- to 650-ft water depth) to offshore deepwater operations (>2,600 ft). Production from these operations is now less than 20%. By 2007, it is projected that as much as 70% of the U.S. oil production will be from deepwater operations. The crude oil from these deep wells is more polar, increasing the amount of dissolved hydrocarbons in the produced water. Existing physical/chemical treatment technologies used to remove dispersed oil from produced water will not remove dissolved organics.

This project, funded by the Office of Fossil Energy, is aimed at devising compact, low-cost, efficient treatment processes to comply with current and future water quality regulations. It is an extension of previous research to improve the applicability of ozonation for treating organics and will help address the petroleum industry-wide problem of handling soluble organics from deepwater operations. The goal of this project is to maximize oxidation of water-soluble organics during a single-pass operation. The project investigates (1) producing oxidants by electrochemical and sonochemical methods, (2) increasing the mass-transfer rate by forming microbubbles during ozone injection into the produced water, and (3) using ultraviolet irradiation to enhance the reaction (if needed).

5.6.2 Progress

To date, bench testing has been conducted with three groups of target compounds in high-ionic-strength aqueous solutions: (1) BTEX, (2) hexanoic acid, and (3) a simulated produced water prepared by contacting crude oil with saltwater. This testing has determined the following:

- Sonochemical oxidation can be effective in destroying some compounds such as BTEX; however, no destruction of hexanoic acid was measured. Further testing of the sonochemical technique is not warranted at this time.
- Effective destruction of hexane-extractable materials can be achieved by ozonation in a reasonable time period (less than 5 min). Further testing is warranted.
- Electrostatic spraying is not effective for treatment of high-ionic-strength solutions such as produced water.
- Ultraviolet irradiation is needed for significant destruction of BTEX by ozonation but does not significantly improve ozonation of simulated produced water.
- The ozonation of hexanoic acid is highly pH dependent. This finding could have significant processing implications.

5.7 ELECTRICALLY DRIVEN TECHNOLOGIES FOR RADIOACTIVE AEROSOL ABATEMENT (D. W. DePaoli, C. Tsouris, and C. H. Mattus)

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Summary: Studies have been initiated in collaboration with The University of Texas to study the effects of electric and acoustic fields on the interactions of aerosol particles.

5.7.1 Purpose and Scope

The objective of this research program, funded by the EMSP and conducted in collaboration with O. A. Ezekoye of The University of Texas at Austin, is to develop an improved understanding of how electrically driven processes (including electrocoalescence, acoustic agglomeration, and electric filtration) may be employed to efficiently treat problems caused by the formation of aerosols during DOE waste treatment operations. The production of aerosols during treatment and retrieval operations in radioactive waste tanks presents significant problems of cost, worker exposure, potential for release, and increased waste volume. Electrically driven technologies offer promise as remote methods for improved treatment; however, existing theoretical models are not suitable for performance prediction and design.

In most particulate collection technology, the marginal collection efficiency increases as the aerosol to be separated increases in size. We are investigating mechanisms for increasing the size of particles in an effluent stream as a preprocessing step. Our work is aimed at employing recent advances in theoretical approaches and experimental techniques to improve our understanding of

how electrical and acoustic methods may be employed most efficiently—alone or in tandem—to tackle aerosol problems. The fundamental understanding achieved may provide the basis for development of innovative new approaches and for optimizing removal processes.

5.7.2 Progress

O. A. Ezekoye recently represented this project at an EMSP/TFA Workshop in Richland, Washington. This was a valuable meeting, describing in detail the problems associated with tank waste retrieval and treatment and discussing the relevance of the EMSP projects to these problems. Washable ceramic and fritted metal filters have been identified as the primary treatment technology for aerosol loading in tank off-gas. Therefore, the DOE end users have not determined electrically driven aerosol treatment to be a high-priority item for tank waste treatment. However, through discussions with Mike Terry, Safety Technical Integration Manager for TFA, an alternative high-priority need was identified—aerosols produced from calcining operations. Experimental and theoretical investigations will be conducted for generic process situations with both types of waste streams in mind, focusing on the capability for removal of aerosols of the size distribution, concentration, and density characteristic of those applications.

5.8 IMPROVED DECONTAMINATION: INTERFACIAL, TRANSPORT, AND CHEMICAL PROPERTIES OF AQUEOUS SURFACTANT CLEANERS (D. W. DePaoli, R. M. Counce, M. Z.-C. Hu, and A. W. Rowe)

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Summary: Laboratory-scale experimentation is under way to determine improved means for decontamination using aqueous surfactant cleaners. Studies have shown that the removal of oil from metal surfaces is highly dependent on process conditions. In addition, we have found that through a simple modification of process conditions, we can greatly improve the speed of oil removal.

5.8.1 Purpose and Scope

This investigation, funded by the EMSP, is focused on decontamination using environmentally benign aqueous solutions, specifically the removal of organics and associated radionuclide and heavy metal contaminants by surfactants. Aqueous-based solutions promise several advantages for decontamination processes, including low hazard potential, low cost, and reduced secondary waste volume through solvent recycle, solvent degradation, and/or incineration.

The work is intended to provide an understanding of interfacial, transport, and chemical processes that govern the effectiveness of aqueous-based surfactant solutions for decontamination of surfaces. In addition, efficient means for separation of waste materials from aqueous-based cleaners will be investigated. It is intended that the understanding developed in this work will be applied to decontamination/decommissioning tasks by laboratory testing of samples from contaminated DOE sites and that the tests will provide the basis for improved approaches to the removal of organic contamination.

5.8.2 Progress

R. M. Counce recently represented this project at the EMSP/D&D Workshop at Savannah River, a useful meeting that described in detail the problems associated with decontamination and decommissioning activities and discussed the relevance of the EMSP projects to these problems. Although interest in this work was expressed by end users, no ties to specific applications have yet been made.

Bench-scale experiments have been carried out to investigate the removal of oil from surfaces using aqueous anionic, cationic, and nonionic surfactant solutions. The studies involved measurements of detachment time of single oil droplets from stainless steel coupon surfaces with varied solution chemistry. The following are highlights of the results obtained to date.

1. Droplet detachment time is significantly affected by pH, surfactant type, and surfactant concentration.
2. A simple modification has been discovered that drastically decreases droplet removal time (nearly two orders of magnitude faster removal with one surfactant); an invention disclosure is in preparation.
3. Similar trends were obtained with single-droplet bench experiments and tests conducted using prototypic commercial cleaning equipment. This suggests that miniature single-droplet experiments can be used effectively in a manner similar to combinatorial chemistry for rapid optimization of cleaning strategies with minimal investment of time and equipment and with low waste production.

5.9 PUBLICATIONS

M. Z.-C. Hu, J. T. Zielke, J.-S. Lin, and C. H. Byers, "Small-Angle X-Ray Scattering Studies of Early-Stage Colloids Formation by Thermohydrolytic Polymerization of Aqueous Zirconyl Salt Solutions," *J. Mater. Res.* **14**, 1-11 (1999).

- M. Z.-C. Hu, E. A. Payzant, and C. H. Byers, "Formation of Monodispersed Colloids and Sol-Gels via Homogeneous Nucleation and Growth in Inorganic Salt Solutions of Mixed Solvents," *J. Colloid Interface. Sci.*, submitted.
- M. Z.-C. Hu, J. T. Zielke, C. H. Byers, J.-S. Lin, and M. T. Harris, "Probing the Early-Stage/Rapid Processes in Hydrolysis and Condensation of Metal Alkoxides," *J. Mater. Sci.*, submitted.
- M. Z.-C. Hu, G. A. Miller, E. A. Payzant, and C. J. Rawn, "Wet Chemical Synthesis of Monodispersed Barium Titanate Particles: I. Homogeneous Coprecipitation of Inorganic Salts," submitted for publication in *J. Powder Technol.*, July issue (1999).
- M. Z.-C. Hu, V. Kurian, E. A. Payzant, C. J. Rawn, and R. H. Hunt, "Wet Chemical Synthesis of Monodispersed Barium Titanate Particles: II. Hydrothermal Conversion of TiO_2 Microspheres to Nanocrystalline BaTiO_3 ," submitted for publication in *J. Powder Technol.*, July issue (1999).
- S. Li, W. Jin, P. Huang, N. Xu, J. Shi, M. Z.-C. Hu, and Y. H. Ma, "Perovskite-Related ZrO_2 -Doped $\text{SrCo}_{0.4}\text{Fe}_{0.6}\text{O}_3$ Membrane for Oxygen Permeation," *AIChE J.* **45**, 276-84 (1999).
- S. Relle, S. B. Grant, and C. Tsouris, "Diffusional Coagulation of Superparamagnetic Particles in the Presence of an External Magnetic Field," submitted for publication in *Physica A*.
- K. Subramaniam, S. Yiacoumi, and C. Tsouris, "Sorption of Copper by Inorganic Particles—Equilibrium, Kinetics, and Particle Interactions: Experimental," submitted for publication in *Colloids and Surfaces*.
- C. Tsouris, D. W. DePaoli, J. T. Shor, M. Z.-C. Hu, and T.-Y. Ying, "Electrocoagulation for Magnetic Seeding of Colloidal Particles," submitted for publication in *Colloids and Surfaces*.
- C. Tsouris and J. Dong, "Effects of Electric Fields on Phase Inversion of Liquid-Liquid Dispersions," submitted for publication in *Chemical Engineering Science*.
- C. Tsouris, A. P. Borole, E. N. Kaufman, and D. W. DePaoli, "An Electrically Driven Gas-Liquid-Liquid Contactor for Bioreactor and Other Applications," accepted for publication in *Industrial and Engineering Chemistry Research*.
- N. Xu, Z. Shi, Y. Fan, J. Dong, J. Shi, and M. Z.-C. Hu, "Effect of TiO_2 Particle Size on Photocatalytic Degradation of Methylene Blue in Aqueous Suspensions," *Ind. Eng. Chem. Res.* **38**, 373-79 (1999).
- T.-Y. Ying, S. Yiacoumi, and C. Tsouris, "High-Gradient Magnetically Seeded Filtration," accepted for publication in *Chemical Engineering Science* (1999).

6. FLUID STRUCTURE AND PROPERTIES

H. D. Cochran

6.1 INTERACTIONS OF SOLUTES, SOLVENTS, AND SURFACES (H. D. Cochran, H. J. Dai, H.-C. Li, and K. D. Heath)

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Summary: Molecular-based studies performed on systems with supercritical solvents include X-ray and neutron-scattering experiments, molecular simulations, and integral equation theory to pursue fundamental understanding of how they behave in practical separations processes.

6.1.1 Objective

This program focuses on our fundamental interest in understanding the practical behavior of separation processes in terms of the underlying molecular interactions. Currently, the work focuses on systems with supercritical solvents and systems with surfactants that form micelles.

6.1.2 Progress

K. D. Heath has modified the apparatus for studying the production of aqueous microdispersions in supercritical CO₂ by pulsed, high-intensity electric fields to enable quantitative measurements of mass-transfer performance to be made, using the extraction of ethanol from ethanol-water solutions as the model system for study. Equipment has been added for measuring and totaling CO₂ mass flow and for condensing, weighing, and analyzing the ethanol-water extract.

A proposal based on this work, "Energy Efficient Separations for Biofuel Ethanol," has been submitted to DOE.

Efforts by H.-C. Li and H. J. Dai have not produced definitive evidence for the existence of micelles in molten salt systems at near-ambient temperatures. Neither SAXS nor neutron-scattering experiments were conclusive. Repetition of the neutron-scattering experiments with deuterated solute (replacing undeuterated solute in the previous experiments) may be undertaken early in the next quarter. Without definitive evidence of the existence of micelles, we will redirect our efforts in other areas.

Our paper, "Supercritical Carbon Dioxide Extraction of Lipids from *Pythium irregulare*," has been accepted for publication.

6.2 MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCRITICAL CO₂ (P. T. Cummings, H. D. Cochran, G. D. Wignall, J. M. DeSimone, E. J. Beckman, Yu. B. Melnichenko, S. T. Cui, S. Salaniwal, and K. D. Heath)

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Summary: This multi-institutional project aims to develop a molecular understanding of reverse micelles in supercritical carbon dioxide through small-angle scattering experiments and molecular simulation calculations and, in particular, to determine what molecular characteristics lead to successful surfactants for this application.

6.2.1 Objective

The aim of this multi-institutional project is to develop a molecular understanding of reverse micelles in supercritical carbon dioxide through small-angle scattering experiments and molecular simulation calculations and, in particular, to determine what molecular characteristics lead to successful surfactants for this application.

6.2.2 Progress

Molecular dynamics simulations of reverse micelles with aqueous cores in supercritical carbon dioxide have continued. We have made observations during the transient period of aggregation of micelles from surfactant and water molecules. We have quantified the diffusion coefficients of aggregates of smaller than equilibrium size, the frequency of their collisions with one another, and the frequency of their coalescence to form larger aggregates.

Our paper, "Vapor-Liquid Phase Coexistence of Alkane-CO₂ and Perfluoroalkane-CO₂ Mixtures," has been accepted for publication.

6.3 STRUCTURE AND PROPERTIES OF CHAIN MOLECULE SYSTEMS UNDER SHEAR (H. D. Cochran, P. T. Cummings, S.-T. Cui, H.-J. Dai, J. D. Moore, Yu. V. Kalyuzhyi, and M. D. Dadmun)

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Summary: This program employs experiments, molecular simulations, and theory to understand the structure and properties of systems of long-chain molecules under homogeneous shear (planar Couette flow).

6.3.1 Objective

The aim of this program is to develop techniques for quantitative, molecular-based prediction of the structure and properties of systems of long-chain molecules undergoing shear flow through coarse graining of accurate, atomistic simulations of shorter-chain systems and coarse graining based on theory and verified by careful small-angle light scattering (SALS), SAXS, and small-angle neutron-scattering (SANS) experiments on sheared systems.

6.3.2 Progress

H. J. Dai has been assembling the shear cell for SALS studies of chain molecule systems at high strain rates. The spindle has been balanced; the drive system has been installed and initially tested; and components of the stress-measuring instrumentation have been fabricated. Following allocation of equipment funds, the specifications for the high-sensitivity charge-coupled device camera have been completed; vendors have been surveyed; and a purchase requisition is being prepared. We anticipate the initial testing of the completed system will take place during the summer of 1999.

Nonequilibrium molecular dynamics simulations of systems of long-chain molecules under shear have continued. Both the transient startup rheological behavior and the steady-state viscosity versus strain rate have been studied.

Equilibrium molecular dynamics simulations using another nonequilibrium potential model have been initiated. The current potential model is expected to yield a more accurate fluid structure at high strain rates than the previously tested model.

Our paper, "Molecular Dynamics Simulation of the Rheological and Dynamical Properties of a Model Alkane Fluid Under Confinement," has been accepted for publication.

A proposal based on this work, "Pore-Scale Modeling of Thermodynamics and Transport of Fluids in Porous Media," has been submitted to DOE.

6.4 PUBLICATIONS

S. T. Cui, H. D. Cochran, and P. T. Cummings, "Vapor-Liquid Phase Coexistence of Alkane-CO₂ and Perfluoroalkane-CO₂ Mixtures," *J. Phys. Chem. B*, accepted.

T. H. Walker, H. D. Cochran, G. J. Hulbert, and L. R. Wilhelm, "Supercritical Carbon Dioxide Extraction of Lipids from *Pythium irregulare*," *J. Assoc. Oil Chem. Soc.*, accepted.

S. T. Cui, P. T. Cummings, and H. D. Cochran, "Molecular Dynamics Simulation of the Rheological and Dynamical Properties of a Model Alkane Fluid Under Confinement," *J. Chem. Phys.*, accepted (1999).

7. BIOTECHNOLOGY RESEARCH

E. Greenbaum

7.1 KINETICS OF ENZYME-CATALYZED PROCESSES (E. Greenbaum, J. Woodward, J. W. Lee, and B. R. Evans)

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Summary: This research studies the fundamental reactions of photosynthesis and the conversion of light energy into chemical energy. During the period, the potential generated by Photosystem I (PSI) molecules oriented on gold substrate was measured.

7.1.1 Purpose and Scope

The purpose of this research program is to study the fundamental reactions of photosynthesis and conversion of light energy into chemical energy. Sustained simultaneous photoevolution of molecular hydrogen and oxygen is studied as a model photosynthetic reaction in which the energy-rich product produced is molecular hydrogen rather than a carbon dioxide fixation compound. Basic issues investigated include the molecular mechanisms of gas evolution, the thermodynamic limits of photosynthesis, and the minimum number of light reactions required to split water to hydrogen and oxygen. Fundamental studies on the enzymology of cellulase are also being performed.

7.1.2 Progress

During this period, we have measured the potential generated by Photosystem I (PSI) molecules oriented on gold substrate. When the light is on, the potentials of PSI acceptors (FA and FB) are negative after the capture of electrons. While in the dark, the potentials of PSIs are positive. These results are consistent with previous studies showing that PSI complexes possess positively charged domains, which interact electrostatically with the negatively charged domain of plastocyanin. A cross section of the PSI potential at dark reveals a positive potential with a lower value at the center than at the two sides. In all our measurements, the potential of one side is always slightly higher than the other. We have measured three locations on each cross section: on the lower side, the center, and the higher side. The average potentials of 12 PSIs (light-off) at these three locations are 0.77 ± 0.14 V, 0.62 ± 0.08 V, and 0.99 ± 0.20 V. The average potentials of 22 PSIs

(light-on) at the three locations are -0.47 ± 0.26 V, -0.41 ± 0.24 V, and -0.59 ± 0.26 V. A higher standard deviation is observed for the measurements of PSI potential upon light incident—probably because the degrees of electron decay from various PSIs are different. Since the electron was not transferred further in our system after it reached the terminal electron acceptors (FA and FB), it will eventually decay. We have also measured the potential difference on the same PSI between light-on and light-off. The average potential differences of four PSIs at the preceding three locations are -1.13 ± 0.14 V, -0.97 ± 0.04 V, and -1.20 ± 0.19 V. These results are consistent with those from previous research indicating that the terminal electron acceptor FB is located higher in PSI than the FA.

A plasmid—containing a construct consisting of a cellulose-binding domain (CBD) from *cenA* of *Cellulomonas fimi* fused to a histidine tag—was obtained from Novogen, Inc., and expressed in *Escherichia coli*. Recombinant CBD was isolated from the periplasmic fraction of a 4-h induced culture. Upon induction for 20 h, large amounts of CBD were found in the culture media as well as in the periplasmic fraction. This CBD was purified by ion-exchange chromatography and determined to bind to crystalline cellulose. The CBD inhibited hydrolysis of microcrystalline cellulose by *Trichoderma reesei* CBH I.

7.2 RENEWABLE HYDROGEN PRODUCTION BY PHOTOSYNTHETIC WATER SPLITTING (E. Greenbaum, J. W. Lee, and S. L. Blankenship)

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Summary: This task is focused on the production of renewable hydrogen by photosynthetic water splitting. During the reporting period, significant progress was made in demonstrating experimentally the concept that overall photosynthetic efficiency of an algal population can be improved by reduction of the size of light-harvesting antennae.

7.2.1 Purpose and Scope

The purpose of this research program is the production of renewable hydrogen by photosynthetic water splitting. Experiments on the production of hydrogen and oxygen with a view towards the design and development of a real-world process system are being performed. An understanding of the limitations of the photosynthetic process, the light saturation curves, and the long-term stability and endurance of microalgae are under investigation.

7.2.2 Progress

Our recent publication (Greenbaum and Lee, 1998, *Biohydrogen*, pp. 235–41) presents a concept of linearization of photosynthetic light saturation curves. The premise is that the overall photosynthetic efficiency of an algal population can be improved by reduction of light-harvesting antenna size. In full sunlight ($2000 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), a kinetic imbalance exists between the rate of photon excitation of photosynthetic reaction centers and the ability of the thermally activated electron-transport chains to process photogenerated electrons. The reaction centers can receive photoexcitation at a rate of about 2000/s, whereas the operation of the electron-transport chain can be only on the order of about 200/s or less. Therefore, normal photosynthesis saturates at a level much lower than full sunlight, typically about 10%. Reduction of light-harvesting antenna size can effectively reduce the rate of photon absorption per reaction center and allow actinic photons to penetrate deeper into the algal culture, thus improving the overall efficiency of photosynthetic utilization of sunlight.

During this reporting period, significant research progress has been made to experimentally demonstrate this important concept. Antenna-deficient mutants of *Chlamydomonas* DSP521 and wild-type DES15 were comparatively assayed for photoassimilation of CO_2 under various actinic intensities. A portion of the antenna chlorophyll molecules are removed in DSP521 through a genetic mutation. Therefore, DSP521 has fewer chlorophyll molecules per reaction center than DES15. These algal strains were obtained from our collaborator, Professor Laurie Mets of the University of Chicago, and grown under a light intensity of about $20 \text{ E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ in minimal-plus-acetate medium. The rationale for growing these strains photoheterotrophically is that the selection pressure for algal cells to make antenna would be minimal under such a growth condition.

When the cultures grew to a cell density of about 10^6 cells/mL, the algal cells were harvested by gentle centrifugation (3000 rpm). They were then washed and resuspended in fresh minimal medium for photosynthetic assays.

The CO_2 fixation assays were performed with 700 ppm CO_2 in helium or air using our unique dual-reactor-flow detection system. The actinic illumination was provided by a red (peak wavelength at 670 nm) light-emitting diode (LED) light source that was controlled with a computerized step motor. Because of the automatic control of the LED light source by the computerized step motor, precise and reproducible step functions of actinic intensity were generated. The actinic intensity was monitored and recorded by a computer simultaneously with the rates of CO_2 fixation. Analysis of experimental data has now shown that the maximal rate of CO_2 fixation in DSP521 with 700 ppm CO_2 under air was about two times higher [$187 \mu\text{mol}\cdot\text{h}^{-1}\cdot(\text{mg chl})^{-1}$] than

that of the wild type, DES15 [$95 \mu\text{mol}\cdot\text{h}^{-1}\cdot(\text{mg chl})^{-1}$]. DSP521 also had significantly more resistance to photoinhibition than did the wild type. The simultaneous monitoring of CO_2 photoassimilation and actinic intensity showed that the photosynthetic activity in the wild type was photoinhibited almost completely when the LED actinic light reached its full intensity [red (peak) wavelength: 670 nm, photons: $2000 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$], while DSP521 remained about 25% of its maximal photosynthetic activity. The photoinhibited wild-type cells released more CO_2 by respiration than by CO_2 fixation, while DSP521 was still capable of photosynthesizing. These are important results since they demonstrate that reduction of photosynthetic antenna size in green algae can indeed improve the overall efficiency in CO_2 fixation and provide resistance to photoinhibition.

Photoassimilation of CO_2 was also measured with 700 ppm CO_2 in helium. The maximal rate of CO_2 photoassimilation in DSP521 [$165 \mu\text{mol}\cdot\text{h}^{-1}\cdot(\text{mg chl})^{-1}$] was about 37% higher than that in DES15 [$120 \mu\text{mol}\cdot\text{h}^{-1}\cdot(\text{mg chl})^{-1}$]. However, no dramatic photoinhibition was observed in either DSP521 and DES15 under the anaerobic (helium) condition. This is expected since photoinhibition results largely from the formation of singlet oxygen, which can react with many biomolecules and destroy their functionality. The anaerobic condition limits the formation of this destructive species. Based on the measured rates of photosynthesis, the antenna size in DSP521 was estimated to be about 30–50% smaller than that in DES15. More experimental studies are under way to verify these findings.

7.3 FLUOROMETRIC TISSUE-BASED BIOSENSORS (E. Greenbaum and C. A. Woodward)

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Summary: Initial preparations have begun on the development of fluorometric tissue-based biosensors for chemical and biological warfare agents.

7.3.1 Purpose and Scope

The purpose of this research project is the construction of biosensors for chemical and biological warfare agents. It is based on the signature fluorescence emission pattern from unicellular algae and the change in that pattern upon exposure to toxic agents.

7.3.2 Progress

This project began March 1, 1999. Initial reorganization of the laboratory has begun for the development of fluorometric techniques to assess the effects of chemical toxins on tissue-based

biosensors. The biosensors will be composed of viable photosynthetic organisms in a low-water environment. The organisms for the biosensor will be chosen from a list of eukaryotic algae and prokaryotic cyanobacteria, based on their ability to use CO₂ as a sole carbon source and their resistance to anhydrous stress, which make them ideally suited for the rigors of biosensor development. The unicellular alga *Chlorella* and several axenic cultures of the cyanobacteria *Nostoc* have been inoculated into appropriate minimal media and are growing in the laboratory in preparation for upcoming experiments. The microorganisms will be monitored for their response to desiccation and immobilization as well as to chemical toxins. The instrumentation necessary for these assay measurements includes a chlorophyll fluorescence monitor (Morgan Scientific, Inc.) and a Clark oxygen-monitoring electrode (Hansatech Instruments, Ltd.), which have been set up and calibrated in the laboratory. The characteristic fluorescence emission pattern of cultures of *Chlorella* with a chlorophyll concentration of 5 g/mL has been recorded using the fluorescence monitor. It will be possible to make direct comparisons between fluorescence patterns of healthy cultures and cultures contacted with chemicals such as cyanide and dibutylsulfide that stress their capabilities for photosynthesis. The viability of the algal electron-transport system can be monitored by measuring the oxygen generated when the algae are illuminated periodically.

Oxygen production will, therefore, be a good indicator of the biological capability of the algae both during sensor development and during chemical treatment. The oxygen electrode consists of a silver-anode/platinum-cathode electrode chamber connected to a dc power supply and transducer with a digital voltage output. Distilled water with known oxygen content is placed in the electrode compartment, and the voltage produced is recorded. The voltage output from the electrode has been calibrated and is linear in response to moles of O₂ per milliliter of water in the range 0–0.26. These experiments are a prelude to the development of a device that will house immobilized photosynthetic organisms, which can be monitored for characteristic patterns of fluorescence alterations in response to stress.

7.4 CELLULASES WITH ENHANCED ACTIVITY (B. R. Evans and J. Woodward)

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Summary: A thermophilic endoglucanase with high activity on soluble cellulose and two different CBDs were incubated with insoluble cellulose to determine if the endoglucanase would be able to bind to and hydrolyze insoluble cellulose by synergistic interaction with the CBDs. No

hydrolysis of the insoluble cellulose was observed, indicating that presence of the CBDs in the reaction was not sufficient to impart activity to the endoglucanase.

7.4.1 Purpose and Scope

To improve biocatalysts for industrial conversion of lignocellulosic materials into fermentable sugars, an increase in the catalytic rate of hydrolysis of cellulose is targeted. The mechanisms of cellulase action on cellulose fibers and synergy between cellulases are still unclear. To resolve these problems, cellulases from both mesophilic and extremophilic microorganisms are being studied and their interactions with insoluble cellulose and cellulose fibers examined.

7.4.2 Progress

An endoglucanase from *Thermotoga maritima* has high activity on soluble cellulose but lacks a CBD. As certain bacterial cellulases occur as cellulosome complexes formed from CBD scaffolds and endoglucanase catalytic domains, the addition of exogenous CBD to this endoglucanase during hydrolysis of microcrystalline cellulose was attempted. Neither the addition of the cen A CBD nor the addition of a recombinant clostridial CBD obtained from Sigma improved the hydrolytic activity of this endoglucanase upon microcrystalline cellulose.

7.5 ENZYMATIC HYDROGEN PRODUCTION FROM BIOMASS (H. M. O'Neill, A. L. Larsen, and J. Woodward)

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Summary: Currently, work is focused on methods to increase the efficiency of the enzymatic production of hydrogen from glucose.

7.5.1 Purpose and Scope

The future use of hydrogen as a renewable fuel is receiving wide attention in both political and technical circles. An enzymatic in vitro process for the production of hydrogen from biomass is currently under investigation. This process centers on two NADP⁺-dependent enzymes, glucose dehydrogenase (GDH) from *Thermoplasma acidophilum* and hydrogenase from *Pyrococcus furiosus*.

7.5.2 Progress

NADP⁺ is degraded during the glucose GDH/hydrogenase-coupled reaction. Further addition of NADP⁺ restores the rate of hydrogen production. Therefore, the immediate goal was to investigate methods to stabilize the NADP⁺ moiety. It was decided to immobilize the NADP⁺ on a

high-molecular-weight soluble support. To carry out this procedure, it was first necessary to modify the NADP⁺ to allow it to react with a polymer such as dextran or poly-L-lysine. The first approach was to convert an NAD⁺ derivative (N⁶-([aminohexyl]carbamoylmethyl)-nicotinamide adenine dinucleotide) to the corresponding NADP⁺ derivative by enzymatic means using NAD⁺ kinase. The NAD⁺ derivative is commercially available and reacts with cyanogen bromide-activated dextran. The rate of conversion was slow even when NAD⁺ was the substrate. It was decided that this method was too inefficient. Another approach tried was to use imido-ester cross-linking agents, which react with free amine groups to form stable covalent bonds. NADP⁺ has a free amine group attached to the adenine ring; it was cross-linked with the ϵ NH₂ groups of lysine residues in gelatin. The adduct formed was stable with storage at 4°C and retained catalytic activity.

The most successful method tried has been the attachment of NADP⁺ to the soluble polymer poly-L-lysine using the cross-linker glutaraldehyde. The resulting NADP⁺ derivative is catalytically active. It retains activity following storage at 4°C over several days and after incubation at 55°C for 16 h. The activity of the NADP⁺ derivative was measured in a GDH-based assay. The reactivity of the immobilized NADP⁺ has also been tested in the GDH/hydrogenase-coupled reaction in the presence of 100 μ mol glucose. A fourfold increase in the initial rate of H₂ evolution and a 1.5-fold increase in the final yield were recorded with immobilized NADP⁺ compared with the free cofactor. Further work will be carried out to fully characterize the NADP⁺ derivative.

It is of interest to immobilize the enzymes involved in the enzymatic production of hydrogen. Invertase from *Canida utilis* was immobilized within propylene glycol alginate gelatin spheres. The stability and activity of the immobilized enzyme were compared with those of the free enzyme under different reaction conditions. The immobilized enzyme was more stable than the free enzyme at 55 and 65°C over 3 days. It also retained greater activity when assayed at temperatures up to 85°C. The pH optimum of the immobilized invertase was pH 5.0 compared with a pH 4.0 optimum for the free enzyme. The K_m for the immobilized enzyme is 64.9 mM compared with 14 mM for the free enzyme. No leakage of the enzyme from the beads occurred over a 6-day period at 55°C. The gelatin beads could be dehydrated and rehydrated at least seven times without a loss in activity.

GDH from *Solfolobus solfataricus* was used in place of *Thermosplasma acidophilum* GDH for the enzymatic production of hydrogen from glucose. This enzyme is thought to be more stable than *T. acidophilum* at high temperature. Experiments were carried out to find the optimal conditions for the production of hydrogen in a hydrogenase-coupled assay. The effect of varying substrate concentration and cofactor concentration on the rate of hydrogen production was examined.

The effect of pH and temperature was also examined. Higher concentrations of glucose (50 mM) appear to inhibit the production of hydrogen. A similar effect was seen for NADP⁺ (1 mM). The initial rate of hydrogen production was affected by temperature; however, the overall amount of hydrogen produced in all the experiments was very similar. The optimal pH for the reaction was found to be pH 7.0.

A full characterization of the *T. acidophilum* GDH/hydrogenase-coupled reaction will be carried out to determine the effect of high glucose concentration and NADP⁺ concentration on the rate of hydrogen evolution. This will also allow a comparison of the *S. solfataricus* and *T. acidophilum* GDHs. Work is currently under way to immobilize GDH within propylene glycol alginate gelatin beads.

7.6 HYDROGEN PRODUCTION FROM IRON (J. P. Getty and J. Woodward)

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Summary: Research has focused on the nonenzymatic production of hydrogen, specifically the optimization of hydrogen generation by an iron-powder catalyst under anaerobic conditions.

7.6.1 Purpose and Scope

The intent of this project is to identify a system of hydrogen generation for commercial vehicle transportation.

7.6.2 Progress

In a novel reaction, sustained hydrogen production has been observed for over 33 days in the presence of gluconic acid. The hydrogen generated has been sufficient to power a digital clock over this period of time. It has been determined that gluconic acid is oxidized during the reaction, adding support to our hypothesis that the catalyst is regenerated by the presence of the acid.

7.7 PUBLICATIONS

- V. A. Boichenko, E. Greenbaum, and M. Seibert, "Hydrogen Production by Photosynthetic Microorganisms," in *Photoconversion of Solar Energy, Volume III: Molecular to Global Photosynthesis*, ed. M. D. Archer and J. Barber, Imperial College Press, 1999, in press.
- B. R. Evans and J. Woodward, "Protein Injury Prevention by Antioxidants," submitted for publication as a chapter in *Biomolecular Injury: Causes and Prevention of Toxicity*, ed. A. Wiseman, P. Goldfarb, T. Ridgeway, and H. Wiseman, John Wiley and Sons, New York.

7.8 PRESENTATIONS

- E. Greenbaum, "Application of Photosynthesis to Renewable Hydrogen Production and Atmospheric Carbon Dioxide Reduction," presented to the Joint Delegation, Japan External Trade Research Organization and Research Institute of Innovative Technology for the Earth, Oak Ridge, Tennessee, February 11, 1999.
- E. Greenbaum, I. Lee, and J. W. Lee, "New Photosynthetic Pathways: Molecular Electronics, CO₂ Reduction, and H₂ Production," contributed presentation at the 43rd Annual Meeting of the Biophysical Society, Baltimore, Maryland, February 13-17, 1999.
- J. W. Lee and E. Greenbaum, "Nanofabrication and Biometallocatalysis," contributed presentation at the 43rd Annual Meeting of the Biophysical Society, Baltimore, Maryland, February 13-17, 1999.
- I. Lee, J. W. Lee, and E. Greenbaum, "Using PSI as Molecular Electronic Devices: Their Electronic and Orientation Control," presented at the Centennial Meeting of the American Physical Society, Atlanta, Georgia, March 20-26, 1999.
- B. R. Evans, J. Zhou, I. Lee, T. L. Poole, and J. Woodward, "Interaction Between Traditional and Novel Hydrolytic Enzymes and Lignocellulose," presented at the 217th National Meeting of the American Chemical Society, Anaheim, California, March 21-25, 1999.
- H. M. O'Neill and J. Woodward, "Applications of Biocatalysts in Hydrogen Production," presented at the 217th National Meeting of the American Chemical Society, Anaheim, California, March 21-25, 1999.

8. MOLECULAR STUDIES

P. T. Cummings

8.1 AQUEOUS ELECTROLYTE SOLUTIONS AT AMBIENT AND SUPERCRITICAL CONDITIONS (P. T. Cummings, A. A. Chialvo, T. Driesner, and I. Borzsák)

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Summary: Calculations exploring the supercooled water behavior of the TIP4P water model continued, and prediction of the vapor-liquid coexistence curve for the TIP4P-FQ water model was concluded.

8.1.1 Purpose and Scope

This project is aimed at developing microscopic-level understanding of aqueous electrolyte solutions using a combination of molecular simulation, statistical mechanical theory, and experimental measurement of vapor-liquid equilibrium and solution densities. The state conditions

of interest range from ambient conditions to high-temperature/high-pressure supercritical conditions (such as those encountered in power plant steam cycles and supercritical water oxidation).

8.1.2 Progress

Ariel Chialvo continued using molecular dynamics to explore the supercooled water behavior for the TIP4P water model in the range of 75 to 150 K, as part of an ongoing collaboration with P. G. Kusalik at Dalhousie University (Canada).

Eric Yezdimer completed calculation of the phase envelope of the TIP4P-FQ model for water using the Gibbs-Duhem integration method of Kofke. A manuscript was in preparation for *Molecular Physics*.

During the quarter, the following paper was accepted for publication in *Chemical Geology*: E. M. Yezdimer, J. Sedlbauer, and R. H. Wood, "Predictions of Thermodynamic Properties at Infinite Dilution of Aqueous Organic Species at High Temperatures via Functional Group Additivity." This paper represents work partially completed by Eric Yezdimer since he joined the group. The following two papers were published: I. Borzsák, and P. T. Cummings, "Molecular Dynamics Simulation of Ice XII," *Chem. Phys. Lett.* **300**, 359–63 (1999), and A. A. Chialvo and P. T. Cummings, "Molecular-Based Modeling of Water and Aqueous Solutions at Supercritical Conditions," *Adv. Chem. Phys.* **109**, 115–205 (1999). The latter was a major invited review paper concerning the field of molecular modeling of high-temperature high-pressure water and aqueous solutions.

The research performed as part of this project was described by P. T. Cummings in a plenary lecture to an international conference: "Molecular Modeling of Water and Aqueous Solutions at High Temperatures and Pressures," XXVIII Winter Meeting on Statistical Physics, Cuernavaca, Mexico, January 6–9, 1999.

8.2 THEORY AND MOLECULAR SIMULATION OF NONEQUILIBRIUM SYSTEMS (P. T. Cummings, A. Baranyai, S. T. Cui, J. D. Moore, and I. Borzsák)

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Summary: The viscosity and viscosity index of various linear and branched alkanes, including a large-scale simulation of C₁₀₀, was continued. The transient time correlation function (TTCF) formalism was under development in our group.

8.2.1 Purpose and Scope

In this project, we study and develop new simulation algorithms for systems away from equilibrium. These algorithms form the basis for the calculation of transport properties using non-equilibrium molecular dynamics.

8.2.2 Progress

Jonathan Moore continued work on the rheology of a C_{100} model polymer melt under shear. Doi Edwards theory was found to be applicable to the stress overshoot in the short polymer chains but only by taking into account the shear-rate dependence of the reptation time. In addition, further analysis of this behavior was made by decomposing the total stress into the contributions from various molecular interactions. The simulations are being performed on the massively parallel Cray T3E supercomputer located at the National Energy Research Supercomputing Center (NERSC) at Lawrence Berkeley National Laboratory, as well as on Cray T3E's located at Cray headquarters in Minnesota and Intel Paragons at ORNL. Moore continued preparation of a manuscript on this work and also continued preparing a technical report on MDVIZ, a molecular dynamics visualization package originally developed by Peter Cummings while at the University of Virginia.

Shengting Cui completed nonequilibrium molecular dynamics calculations of the pair-correlation functions of the soft sphere fluid under shear for comparison with a newly developed integral equation theory being performed by Yuriy Kalyzhnyi. A manuscript on this work was written.

István Borzsák made extensive production runs using parallel computers for a simple fluid using his nonequilibrium molecular dynamics program that calculates the viscosity using the TTCF formalism. The essential data are almost complete and a manuscript will be initiated. He also continued the implementation of the TTCF formalism for fluids of greater industrial importance, namely alkane chains. The first model for these studies is *n-decane*. The code generation is almost complete for serial computers for this model.

8.3 INTEGRAL EQUATION THEORIES OF MOLECULAR FLUIDS (P. T. Cummings, Yu. V. Kalyuzhnyi, and J. N. Herrera)

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Summary: Study of an integral equation theory for nonequilibrium systems was completed.

8.3.1 Purpose and Scope

This project involves the use of integral equation methods to describe molecular fluids and polymers in the dense-liquid regime. The emphasis is on analytically solvable integral equation theories.

8.3.2 Progress

Yu. Kalyuzhnyi completed a detailed study and evaluation of the integral equation theory of Eu and Gan. The theory offers the possibility of calculating structural and rheological properties of systems away from equilibrium.

8.4 MATHEMATICAL MODELING OF BACTERIAL MIGRATION THROUGH POROUS MEDIA WITH APPLICATION TO IN SITU BIOREMEDIATION (P. T. Cummings, R. M. Ford,* K. C. Chen,* and M. Jin*)

Contact: P. T. Cummings
Telephone: (423) 241-4779
Internet: u53@ornl.gov

Summary: Several papers from this completed project appeared.

8.4.1 Purpose and Scope

This project is part of a broad effort at the University of Virginia funded by the IBM Environmental Research Program, with Roseanne Ford and Peter Cummings as coprincipal investigators. The goal of the project is to perform experimental studies and computer simulations of bacterial motion in bulk aqueous phases and in porous media to develop an understanding of the transport processes involved with in situ bioremediation and to subsequently develop mathematical models for these processes. The project funding ended December 31, 1997.

8.4.2 Progress

This project is no longer funded and is being concluded. A final report to the sponsors (IBM) was completed and submitted in October 1998. During the quarter, two papers were published: "Spatial Effect of the Tumbling Frequencies for Motile Bacteria on Cell Balance Equations" and "Perturbation Expansion of Alt's Cell Balance Equations Reduces to Segel's 1d Equations for Shallow Chemoattractant Gradients."

*University of Virginia.

8.5. FUNDAMENTAL CHEMISTRY AND THERMODYNAMICS OF HYDROTHERMAL OXIDATION PROCESSES (J. M. Simonson, R. E. Mesmer, D. J. Wesolowski, P. T. Cummings, and A. A. Chialvo)

Contact: P. T. Cummings
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Summary: The Chialvo-Cummings solvation formalism was applied to electrolyte solutions. Molecular simulation of HCl solutions was continued.

8.5.1 Purpose and Scope

The goal of the project is to use a combination of molecular theory/simulation and experimental measurements to develop a fundamental understanding of the thermophysical properties, phase equilibrium, and reaction processes involved in supercritical water oxidation (a new and promising technique for transforming hazardous organic waste).

8.5.2 Progress

Ariel Chialvo applied the Chialvo-Cummings solvation formalism to model electrolyte solutions, based on integral equation calculations of simple alkali halides. He tested a regression hypothesis currently used by experimentalists and interpreted the microscopic mechanism behind its success. A portion of this work is included in a manuscript under preparation, and a poster is to be presented at the 4th Liquid Matter Conference in Spain in July 1999.

Ariel Chialvo implemented a new approach to the potential of mean-force calculations for aqueous HCl solutions, based on the SPC/E model of water and variations of Hynes and Kusaka's model for the hydronium ion, with the goal of calculating the association constant of HCl at near-critical conditions.

8.6. DEVELOPMENT AND APPLICATION OF FAST COMPUTATIONAL PROTEIN-FOLDING ALGORITHMS USING MASSIVELY PARALLEL SUPERCOMPUTERS (P. T. Cummings, P. H. LoCasio, K. Dill,* and Kai Yue*)

Contact: P. T. Cummings
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Summary: Progress continued to be made in the parallelization of the Geocore algorithm.

*University of California-San Francisco.

8.6.1 Purpose and Scope

The goal of the project is to develop parallel implementations of the Geocore ab initio exhaustive-search protein-folding algorithm and use the parallel version to predict the structures of larger proteins, to improve the performance of the Geocore algorithm, and to develop much faster, less exhaustive algorithms for very large proteins.

8.6.2 Progress

Kai Yue and Phil LoCasio continued development of the Geocore ab initio protein-folding algorithm. A search was initiated for a postdoctoral researcher from the Oak Ridge Institute for Science and Education to participate in this project.

No publications were submitted, accepted, or published from this project during the current quarter.

8.7 MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCRITICAL CARBON DIOXIDE FOR SOLVENT SUBSTITUTION IN THE U.S. CHEMICAL INDUSTRY (P. T. Cummings, H. D. Cochran, S. T. Cui, D. Londono, G. Wignall, A. Habenschuss, E. Beckman,* and J. DeSimone†)

Contact: P. T. Cummings
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Summary: Production runs of our simulation code for reverse micelles were performed for a large-size system (five times larger than our previous simulations) and analyzed.

8.7.1 Purpose and Scope

The aim of this project is to use SAXS and SANS scattering plus complementary molecular dynamics and Monte Carlo simulations to develop a molecular-level understanding of the formation and stability of reverse micelles in supercritical carbon dioxide. The results of this project will contribute to the fundamental knowledge base for the U.S. chemical industry to substitute supercritical CO₂ for many of the toxic or hazardous solvents presently used in most industrial chemical reaction and separation processes. The project is funded by the National Science Foundation (NSF) and the U.S. Environmental Protection Agency.

*University of Pittsburgh.

†University of North Carolina.

8.7.2 Progress

Sumeet Salaniwal performed molecular dynamics simulations of reverse micelles in supercritical CO₂ to study the structural features of the aggregates formed for a large system size composed of 132 water, 30 surfactant, and ~13,000 CO₂ molecules. This is a very large system to simulate; however, our interest in this system is high because it mimics the experimental conditions (ratio of CO₂/water/surfactant and thermodynamic conditions) of the experimental system previously studied by neutron scattering. Two different initial configurations (aggregated and scattered) were used. Salaniwal measured the preliminary structural characteristics of the full system for the initially aggregated condition and began studying the dynamics of aggregation from the point of view of aggregation kinetic theories.

8.8 NANOTECHNOLOGY WITH EMPHASIS ON TRIBOLOGY: A COMBINED EXPERIMENTAL AND SIMULATION STUDY (P. T. Cummings, H. D. Cochran, S. T. Cui, S. Granick,* and G. Grest†)

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Summary: Molecular dynamics simulations of alkanes confined to nanoscale gaps were performed.

8.8.1 Purpose and Scope

This 3-year project, supported by the NSF through the interdisciplinary nanotechnology program, began July 15, 1998. The aim of the project is to undertake a fundamental study of lubrication at nanometer scale, including experiments with surface rheometry and nonequilibrium molecular dynamics simulation. The goals of the research are to achieve overlap in shear rate between experiments and simulations with the same systems, to extend both the experimental and computational efforts to more complicated systems and surface characteristics (including surfaces with chemical and topographical heterogeneity), and to study not only the steady-state shear response of nanotribology systems but also their transient behavior, including the technologically important issues related to adhesion.

*University of Illinois.

†Sandia National Laboratory.

8.8.2 Progress

Clare McCabe, a recent Ph.D. recipient from the University of Sheffield, was recruited as a postdoctoral researcher and arrived in January to participate in this project.

Shengting Cui completed molecular dynamics simulations of alkane liquids confined to nanoscale gaps between surfaces that mimicked the properties of mica and, hence, are closer to experimental confined-alkane systems than any we have previously simulated. Interesting changes in the relaxation time for diffusion perpendicular to the mica surfaces seem to provide some explanation of the remarkable experimental observations (high Newtonian viscosities, transition to Newtonian plateau moved to low strain rate). Although not completely explaining the experimental observations, Cui's work suggests we are moving in the right direction and capturing some of the processes involved in the experiments.

8.9 OTHER IMPORTANT ACTIVITIES

Peter Cummings received notice that he was to be a recipient of a 1999 Lockheed Martin research achievement award, recognizing sustained research achievement.

8.10 PUBLICATIONS

8.10.1 Submitted

Y. Kalyuzhnyi, S. T. Cui, P. T. Cummings, and H. D. Cochran, "Distribution Functions of a Simple Fluid Under Shear. I. Low Shear Rates," *Phys. Rev. E*. (1999).

J. D. Moore, S. T. Cui, P. T. Cummings, and H. D. Cochran, "The Transient Rheology of a Polyethylene Melt Under Shear," *Phys. Rev. Lett.* (1999).

S. T. Cui, P. T. Cummings, and H. D. Cochran, "Molecular Dynamics Simulation of the Rheological Properties of a Model Alkane Fluid Under Confinement," *J. Chem. Phys.* (1999).

8.10.2 Accepted

E. M. Yezdimer, J. Sedlbauer, and R. H. Wood, "Predictions of Thermodynamic Properties at Infinite Dilution of Aqueous Organic Species at High Temperatures via Functional Group Additivity," *Chemical Geology* (1999).

8.10.3 Published

A. A. Chialvo and P. T. Cummings, "Molecular-Based Modeling of Water and Aqueous Solutions at Supercritical Conditions," *Adv. Chem. Phys.* **109**, 115–205 (1999). [invited review article]

- K. C. Chen, R. M. Ford, and P. T. Cummings, "Spatial Effect of the Tumbling Frequencies for Motile Bacteria on Cell Balance Equations," *Chem. Eng. Sci.* **54**, 593-617 (1999).
- K. C. Chen, R. M. Ford, and P. T. Cummings, "Perturbation Expansion of Alt's Cell Balance Equations Reduces to Segel's 1d Equations for Shallow Chemoattractant Gradients," *SIAM J. Appl. Math.* **59**, 35-57 (1999).
- N. Herrera, P. T. Cummings, and H. Ruíz-Estrada, "Static Structure Factor for Simple Liquid Metals," *Molec. Phys.* **96**, 835-47 (1999).
- A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Solvation in High-Temperature Electrolyte Solutions. I. Hydration Shell Behavior from Molecular Simulation," *J. Chem. Phys.* **110**, 1064-74 (1999).
- A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Solvation in High-Temperature Electrolyte Solutions. II. Some Formal Results," *J. Chem. Phys.* **110**, 1075-86 (1999).
- I. Borzsák and P. T. Cummings, "Molecular Dynamics Simulation of Ice XII," *Chem. Phys. Lett.* **300**, 359-63 (1999).
- A. Baranyai and P. T. Cummings, "Steady State Simulation of Planar Elongation Flow by Nonequilibrium Molecular Dynamics," *J. Chem. Phys.* **110**, 42-45 (1999).

8.11 PRESENTATIONS

8.11.1 Invited Seminars

- P. T. Cummings, "Molecular Simulation of Complex Systems Using Massively Parallel Supercomputers," Corporate Research, The Dow Chemical Company, Midland, Michigan, March 4, 1999.
- J. D. Moore and S. Salaniwal, "Understanding and Visualizing Molecular Processes in Industrially Important Systems," AIChE, Knoxville/Oak Ridge Section, January 14, 1999.

8.11.2 Invited Conferences

- P. T. Cummings, "Molecular Modeling of Water and Aqueous Solutions at High Temperatures and Pressures," XXVIII Winter Meeting on Statistical Physics, Cuernavaca, Mexico, January 6-9, 1999.
- P. T. Cummings, "Recent Computational Science and Other Workshops Sponsored by the Federal Government," Interagency Workshop: Vision for Nanotechnology R&D in the Next Decade, Washington, D.C., January 27-29, 1999.
- P. T. Cummings, "Chemical Engineering Applications of Molecular Simulation and Computational Chemistry," 217th American Chemical Society National Meeting, Anaheim, California, March 21-25, 1999.

P. T. Cummings, "Molecular Simulation of Lubricants Confined to Nanoscale Gaps," 217th American Chemical Society National Meeting, Anaheim, California, March 21-25, 1999.

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